A thesis entitled

NITRATE-SELECTIVE ELECTRODES WITH COVALENTLY BOUND SENSORS.

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ABSTRACT

Nitrate determination and ion-selective electrodes, with particular emphasis on the nitrate selective electrode, are reviewed. A new electrode for nitrate has been developed, by covalent attachment of appropriate sensor groups to a robust polymer matrix, with a view to improving the lifetime and the applications of the electrode to include hostile environments. The QAS (I) were prepared as sensor materials.

(1) R' = R" = R"' = ethyl

(2) R' = allyl

R" = R"' = methyl, ethyl, propyl

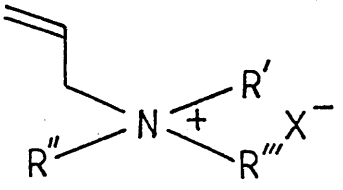
(3) R' = R" = allyl

R"' = methyl, ethyl, propyl, butyl

(4) R' = R" = R"' = allyl

X^- = Cl, Br.

(I)



The production of membranes by cross-linking the sensors (I) with styrene-b-butadiene-b-styrene triblock elastomer (SBS) using a free radical initiated cyclopolymerisation is described.

Various methods of membrane preparation have been investigated, and a convenient one-step solvent casting procedure identified and optimised. A range of membranes has

been prepared and their physical and electroanalytical properties evaluated. The cross-linked density of the polymers was calculated from swelling measurements and the Flory-Rehner equation, the extent of covalent attachment has been derived from Kjeldahl analyses. The performance of the membranes as ion-selective electrodes is presented and discussed. Several electrodes showed fast response, long lifetime and Nernstian behaviour in the range 10^{-1}-10^{-4} mol dm^{-3}, but their selectivity was inferior to present commercial electrodes. A number of materials were introduced as mediators in order to improve the selectivity of the membranes. A possible mediator (o-nitrophenyloctyl ether) was identified and an analogue (o-nitrophenyl-w-undecylenyl ether) prepared which had suitable functionality for covalent attachment to the polymer. Unfortunately the inclusion of this material did not improve the selectivity to chloride and the reasons for this are discussed.

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CHAPTER 1

INTRODUCTION

1.1 Nitrate - Cause for Concern?

The amount of nitrate to which the population is exposed has risen in modern times. The use of agrochemicals and the application of sewage sludge to land, have contributed substantially to this increase; nitrate is also used in foods as a preservative and as an additive in detergents.

The toxicity of nitrite is well recognised. It is known to cause infant methoglobinemia (blue baby syndrome) by oxidation of haemoglobin. Concern is now being expressed about the toxicity of nitrate.[1] Ingested nitrate may be reduced by bacteria to nitrite, which may react *in vivo* with secondary nitrogen compounds to form N-nitroso compounds. Nitrate is present in food and drinking water, secondary amines are ingested in fish and other foods. The reaction is acid catalysed, with an optimum pH 2-4, making the human stomach an ideal location for the production of N-nitroso compounds. These compounds have been recognised as powerful carcinogens for several years.

In view of the action of nitrate *in vivo* the control of nitrate in drinking water, a universal source of nitrate, is now essential. The E.E.C. regulations[2] limit the maximum concentration of nitrate nitrogen (NO_3.N) in

potable water to 11.3 mg N l^{-1}. The current nitrate levels in this country are within the EEC limits, with the possible exception of small areas with naturally occurring high levels of nitrate. However, the levels of nitrate in surface waters fluctuate and may show seasonal maxima which exceed the EEC regulations. At present water authorities are able to blend waters with high nitrate levels, with ground-water supplies which are unpolluted. The agriculturalists defend their use of chemical fertilisers on the basis that only surface waters are affected, but long term monitoring of ground water supplies, such as chalk aquifiers, show that a steady increase in nitrate levels is now apparent.[3]

Thames Water Authority recently published the results of their nitrate studies.[4] They highlighted the need to monitor and control the levels of nitrate and, ultimately, the source of the nitrate pollution. Although the expense incurred by such activities would require substantial investment, the cost of purifying all water supplies by the removal of nitrate should the levels continue to rise, would be enormous in comparison. The current enquiries concerning the problem of acid rain highlight a new type of pollution which involves nitrate and requires a reliable method of monitoring it.

The development of a rapid, versatile, accurate, sensitive, selective and cheap method of nitrate analysis in water and food is now of prime importance for monitoring environmental conditions.

1.2 Methods of Nitrate Analysis

The determination of nitrate can be accomplished by a number of methods: direct spectrophotometry; spectrophotometric methods using chromogenic reagents; reduction of nitrate to ammonia and its detection; enzymatic methods; chromatographic methods; and ion-selective electrode methods. These methods are reviewed in the following pages.

1.2.1 Direct Spectrophotometry

Nitrate ion shows a strong absorption in the far ultra-violet (U.V.) with a peak at 202nm. In the absence of substances which also absorb in this region nitrate can be determined rapidly by direct measurement.

Non-saline waters, low in organic matter, and certain waste waters with high levels of nitrate, are analysed by this method.[5] The range of application is 0.03-2.0 mg l^{-1} in a sample volume of 40ml, the lower limit is dependent on the absence of interferents. The rate of analysis is approximately 10 samples per hour. Light scatter by undissolved particles is a source of error in the U.V. region. Accurate determinations require clear, bright samples; filtration is necessary to eliminate suspended matter and

turbidity. Nitrite absorbs over a similar wavelength range to nitrate, but is removed by the addition of sulphamic acid. Carbonate and hydroxyl ions interfere, but are eliminated by acidification. Dissolved iron and other heavy metals may also cause interference. Chloride and bromide show absorption in the U.V. region of 200nm and below. The detection of nitrate at 210nm is usually chosen to minimise chloride interference, whilst remaining close to the peak maximum for nitrate. A correction for U.V. absorbing substances other than nitrate can be made by measuring absorbance of samples at 2 wavelengths, 210nm and 275nm. Nitrate should have no significant absorbance at the higher wavelength if present in suitable concentrations for this method.

A method for nitrate determination in fresh and suitable estuarine waters, by U.V. absorption was proposed by Brown and Bellinger.[6] Natural organic pollutants, which cause interference in the U.V. region were removed by passing the sample through an ion-exchange resin, chloride levels were controlled by precipitation with silver nitrate, and nitrite was controlled with sulphamic acid. The method allowed 10 to 15 samples per hour to be analysed and was precise and accurate in the range 0.1-3.0mg l^{-1} NO_3.N.

A similar adaptation was used by Rennie et al[7]., for the direct determination of nitrate in raw, potable and waste waters. An activated carbon filter at elevated pH was used to eliminate interference from organic matter. The procedure also removed interferences from a number of cations which were precipitated. The limit of detection was 0.006mg 1^{-1} , and the method compared favourably with established automated methods for a wide range of samples.

Norman and Stucki[8] developed a method for nitrate determination in soil by measuring total absorbance of a sample at 210nm. The nitrate present in the sample was then reduced to non-absorbing species using Raney nickel catalyst in an acid medium. The U.V. absorbance was then determined, the difference between the two readings was attributed to nitrate concentration. Nitrite was removed from samples using sulphamic acid. This method was suitable for 0.45-100μg NO_3.N g^{-1} of soil.

1.2.2 Spectrophotometric Methods using Chromogenic Reagents.

Nitrate can also be determined in various samples by its reaction with an organic reagent to form a coloured compound which is then detected spectrophotometrically.

The reaction of nitrate with sulphosalicylic acid produces a yellow compound in the presence of alkali. The absorbance at 415nm is proportional to nitrate concentration. This method is used for the determination of nitrate in raw, potable and waste waters.[5] The linear

range of the method is 0.003-0.013mg 1^{-1} depending on interference to $<$0.2mg 1^{-1} & the rate of analysis is 1-3 hours for six samples. The main interferents are chloride, orthophosphate, magnesium and manganese (II).

Several methods are reported in the literature[9,10] for the determination of nitrate with 2,6-xylenol (2,6-dimethylphenol). Nitrate in an acidic solution reacts with 2,6-xylenol to form 4-nitro-2,6-xylenol which shows an absorption maximum at 320-324nm. Nitrite and chloride interfere with the reaction.The method is useful for determination of nitrate nitrogen in the parts per million range (5-29ppm)[9].

Andrews[10] also used 2,6-xylenol for the determination of nitrate. The product of the reaction with nitrate was extracted with toluene and the absorbance at 432nm measured. The method was used for concentrations of 0-2.5μg NO_3.N 1^{-1}.

An alternative method[11] for determination of nitrate in water involves the conversion of the extracted phenol to phenoxide before recording the spectrum from 600 to 400nm. The absorbance is defined as the difference between the 428nm peak and the plateau reading between 560-520nm caused by turbidity. A linear relationship between absorbance and nitrate concentration over the range 0-900μg 1^{-1} was reported, with a limit of detection at 50μg 1^{-1}.

2,4-Xylenol has also been used for spectrophotometric determination of nitrate,[12] but the reaction product had the disadvantage of requiring separation by distillation. The reaction with nitrate produced 6-nitro-2,4-xylenol in sulphuric acid which was then distilled into an ammoniacal water/isopropanol mixture. The intense yellow colour produced was monitored at 455nm. Interferences from nitrite and chloride were experienced. The method was used for samples containing 0.05-0.20mg NO_3.N.

A method for the determination of nitrate in plants, soils and waters used the reagent 3,4-dimethylphenol.[13] High tolerance to interferents and applicability to a wide range of NO_3.N values were required for the analysis of such samples. Instantaneous nitration of 3,4-dimethylphenol was achieved in the presence of sulphuric acid. Chloride interference was controlled by precipitation with silver sulphate. The nitration product was distilled into a solution of sodium hydroxide in ethanol, the absorbance of this yellow solution was recorded at 430nm. The method was suitable for plant tissue samples containing 100-2200μg g^{-1} NO_3.N (dry weight), soil samples containing 1-40μg g^{-1} NO_3.N, and water samples containing 1-20μg ml^{-1} NO_3.N.

The method was later modified for the determination of nitrate in rain-water,[14] by removing the distillation step. Nitration occurred instantaneously at $0^{o}C$ in 80% sulphuric acid, the product was extracted into toluene. The extractant was treated with sodium hydroxide to form a coloured product, the absorbance of which was recorded at 432nm. The samples contained 0.5-2.2μg ml^{-1} nitrate.

The advantages of using phenol as a reagent in the determination of nitrate were outlined by Elton-Bott;[15] phenol is cheap and readily available in high purity, the molar absorptivity for the nitro derivative of phenol at 410nm is higher, the tolerance level of the reaction for chloride is also higher. Phenol was used with diluted sulphuric acid to produce nitro-phenols, predominantly ortho and para, which were easily distilled. The method was suitable for plant materials, soils and water with a wide range of nitrate content.

Tanaka et al.[16], described a procedure for the determination of nitrate in vegetable products based on the quantitative nitration of 2-sec-butylphenol in sulphuric acid. The nitration product was extracted, and the absorbance of the yellow compound formed in alkaline medium was measured. The colour reaction was sensitive and stable. The absorbance measured at 418nm obeyed Beers Law between 0.13 to 2.50μg ml^{-1} NO_3.N with a detection limit of 1.3ppm.

The method was not affected by normal interferents from vegetable products and showed high tolerance to nitrite. Nakamura[17] proposed a method of nitrate determination in which chloride ion, in the presence of sulphuric acid (15N), catalysed the reduction of nitrate to nitrite. A selective reaction with a solution of 4,5-dihydroxycoumarin in ethyl acetate produced a coloured compound which was monitored at 382nm. The method showed high tolerance to common interferents but prior determination of nitrite was required. Nitrate was determined rapidly in drinking water samples in the range 0.05-3.0ppm NO_3.N.

Velghe and Claey[18] used 18-19N sulphuric acid, containing chloride ions, to generate the volatile nitrosyl chloride. Reaction with phenol produced p-nitrophenol in equilibrium with the yellow p-benzoquinone monoxime. The coloured compound was monitored at 388nm. The reaction time was approximately 5 min. Interferences from nitrite, sulphate, iron (III) and iodide were minimised or eliminated.

A widely recommended method[5] for the determination of nitrate in the range 20-2000μg l^{-1} NO_3.N, common levels for natural waters, involves the heterogeneous reduction of nitrate with copperised cadmium, zinc, cadmium or cadmium amalgam followed by its diazotisation and coupling with a suitable reagent to form a coloured complex. The

reaction is monitored spectrophotometrically.
The principles of this method have been adapted to continuous flow apparatus to form the basis of commercial autoanalysers for nitrate and total oxidised nitrogen (TON).

An early automatic method for the determination of nitrate and nitrite in fresh or sea water, and soil extracts was described by Henrikson and Selmer-Olsen.[19] Nitrate was reduced with copperised cadmium, the nitrite produced diazotised sulphanilamide which then coupled with N-1-naphthylethylenediamine. The product, a highly coloured azo-dye was detected at 520nm by U.V. spectrophotometry. Predetermination of nitrite was required. A dialyser incorporated into the system prevented clogging of the reductor column. The method was used to determine nitrate in soil extracts in the range 0.2-15mg l^{-1} NO_3.N, and in water samples in the range 0.02-0.8mg l^{-1} NO_3.N.

A manual method for the determination of trace amounts of nitrate in river water[20] involved reduction by a cadmium-copper column, diazotisation of p-aminoacetophenone, and coupling with m-phenylenediamine. The final product was monitored spectrophotometrically at 460nm. The method was used to determine nitrate at levels of $<$ 1mg l^{-1} NO_3.N.

Simultaneous determination of nitrate and nitrite by flow injection analysis was reported by Gine et al.[21]

Nitrate was reduced to nitrite with a copperised cadmium column, the nitrite was diazotised and coupled with N-(1-naphthyl)ethyldiammonium dichloride. The precision was 1.5% in the range 1.0-5.0mg 1^{-1} nitrate, with a sampling rate of $90h^{-1}$. The system was later adapted to a standard addition method for the analysis of nitrate in plant extracts[22]. The standard addition method was required for such samples to overcome matrix effects.

A discrete analyser was used for the determination of nitrate in lake waters[23] containing high concentrations of dissolved organic matter. The method involved reduction with copper and hydrazine, followed by reaction with sulphanilamide and coupling with N-1-naphthylethylene diamine. The copper catalyst was protected from chelation with organic matter, by using excess zinc ions in the system. The total analysis time was below 13min. with a throughput of 240 samples per hour in the range 14-600μg 1^{-1} NO_3.N.

A manual method for the determination of trace amounts of nitrate and nitrite in water was developed[24] in which freshly prepared cadmium sponge was used for the rapid reduction of nitrate to nitrite. At pH2 nitrous acid was formed which diazotised with p-aminoacetophenone which then coupled with N-(1-napthyl)-ethylene diamine. The azo-dye was extracted into butanol in the presence of naphthosulphonic acid and $Al(NO_3)_3$. The absorbance was measured at 550nm. Sodium metaphosphate was used as

a masking agent to prevent interference from other ions.

The determination of nitrate in the concentration range 2-100μg NO_3.N 1^{-1} by manual methods was described by Gaugush and Heath.[25] The method was suitable for small samples 5ml, and the reaction was carried out in a test tube. The reaction involved reduction with cadmium amalgam, reaction with sulphanilamide and N-(1-naphthyl)-ethylenediamine dihydrochloride and measurement of the absorbance at 543nm.

A glassy carbon, column, electrode was used to reduce nitrate in a flow electrolysis method.[26] Nitrite produced on the column was mixed with a sulphanilamide and N-(1-naphthyl)ethylenediamine to produce a coloured product. The absorbance of the product was measured at 540nm. The method was used for nitrate determination in filtered, degassed samples of river water after combination with a phosphate buffer solution containing copper and cadmium ions. Nitrite was predetermined. Low values of nitrate were experienced possibly as a result of further reduction of nitrite by electrolysis.

The methods discussed above provide accurate and sensitive means for the determination of nitrate in various environmental samples. However all the methods require the use of one or more unpleasant reagents; skin contact with

N-(1-naphthyl)ethylenediamine hydrochloride and hydrazine sulphate should be avoided; cadmium metal and its salts are toxic.

Sample preparation and manipulation are important parameters to be considered when selecting a method for routine analyses. The methods described involve multistep reactions which can be time consuming, and costly in reagents. Some involve the use of specialised equipment which increases the rate of sampling, but does not reduce the overall reaction time.

1.2.3 The Reduction of Nitrate to Ammonia

The reduction of nitrate to ammonia is an alternative method of nitrate determination and is also suitable for total oxidized nitrogen.

The recommended method[5] involves the distillation of ammonia from a sample made alkaline with magnesium oxide. Devarda's alloy is then added to the sample and distillation continued. The ammonia produced from the reduction of oxidized nitrogen is absorbed by boric acid solution and titrated against standard acid. It is suitable for nitrate in the range 12-40mg l^{-1} NO_3.N, the analysis time being 1 hour. The method may only be used for nitrate in the absence of nitrite, or if nitrite is predetermined.

1.2.4 Enzymatic Methods

The enzyme nitrate reductase selectively reduces nitrate to nitrite. Although the enzyme is specific, the reaction conditions it requires are complex; a suitable cofactor is required for the reaction to proceed.[27] The radical cation of 1,1'-dimethyl-4,4'-bipyridinium dichloride ($MV^{\bullet+}$) (methyl viologen), which can be generated by the action of $Na_2S_2O_4$ on MV^{2+}, acts as an electron donor - an artificial cofactor. Nitrate was reduced to nitrite in the presence of the radical cation and nitrate reductase. The nitrite produced by the enzyme was monitored by reaction with sulphaniliamide and N-(1-naphthyl)ethylenediamine dichloride to form a coloured azo dye. The reaction was performed in a continuous flow system, with an immobilised enzyme and spectrophotometric detection at 543nm. Samples in the concentration range 17ppb to 7ppm of nitrate were measured with freedom from interference.

An alternative method[28] involved the reduction of nitrate and nitrite to ammonia using nitrate and nitrite reductases and the radical cation $MV^{\bullet+}$as the electron donor. The ammonia generated by the reaction was measured with an air-gap electrode. Nitrate in the range $5\text{-}10^{-5}$ - 1×10^{-2}M was determined by this method but nitrite must be eliminated. Common interferents

do not cause problems, but copper (II) and mercury (II) poison the enzymes.

The analysis of trace amounts of nitrate in water was accomplished with NADH (nicotinamide adenine dinucleotide) dependent nitrate reductase.[29] NADH acted as the electron donor for the enzyme catalysed reduction of nitrate. During the reaction NADH was oxidised to NAD+, and its disappearance was monitored fluorometrically. The range of determination was 50ppb to 7.5ppm.

An enzymatic method for the determination of nitrate in meat and fish products was used by Hamano et al.[30] for the range 10 to 100ppm with a detection limit of 0.5ppm. Nitrate was extracted from meat products with sodium hydroxide and subjected to ultrafiltration. The samples were reduced with respiratory nitrate reductase from E.coli. The resulting nitrite was determined by a diazotisation coupling reaction. The method was relatively free from interference, nitrite did not affect the enzymes.

Kobos et al.[31] used a bacterial membrane electrode for the determination of nitrate. Bacteria containing the necessary enzymes to reduce nitrate to ammonia were positioned on the surface of an ammonia gas sensor supported by a dialysis membrane. The bacterium Azotobacter vinelandii contained the necessary enzymes

and cofactors for the required reactions. Nitrate was reduced to ammonia by a two step process involving nitrate and nitrite reductase. The sensor showed linear response between 1×10^{-5} and 8×10^{-4}M and a lifetime of two weeks. The electrodes showed slow response and recovery times because of their dependence on the diffusion of reagents through the membrane layers.

A major drawback of enzymatic methods is the cost of the enzymes. Immobilised enzymes can be used many times and help to reduce the cost of such methods. However, the selectivity of the reaction depends on the type of enzyme available and its purity. Bacteria and other cells are a useful source of enzymes which are either difficult to isolate, or require complex conditions, but interferences may occur from other reactions which are taking place in the cells.

1.2.5 Chromatographic Methods

Ion chromatography is a relatively new method for the analysis of inorganic ions. The instruments consist of efficient ion - exchange columns through which an eluent is pumped.

A sample is introduced onto the column using an injection valve. Ions from the sample are retained by the column to varying degrees and emerge at characteristic retention times. Suppressor columns are often used to remove cations from the samples and so reduce interference or increase sensitivity.

High performance liquid chromatography (HPLC) has been used to determine traces of inorganic ions.[32] Well-packed analytical columns, containing small rigid anion-exchanger beads at high pressure, were used to achieve efficient separation of several ions. The beads were covered with a methacrylate resin containing quaternary ammonium salts. Suppressor columns containing a strong cation exchanger, divinylbenzene copolymer, were used to exchange all the cations in the eluent for protons. Detection was achieved by a conductivity cell, therefore removal of cations from the sample resulted in low background conductivity at suitable pH. Succinate/hydrogen succinate or adipate/hydrogen adipate were suitable eluents. Phosphate, bromide, nitrate and sulphate ions were separated in 6min. Detection limits were approximately 20μg 1^{-1} for a 200μl sample, and 4μg 1^{-1} when 2ml samples were preconcentrated.

Okada and Kuwamoto[33] used nonsuppressor ion chromatography to separate inorganic ions in environmental samples. The limit of detection for nitrate was 15ppb with potassium hydroxide eluent and a conductivity detector. A problem encountered by this system was column overloading caused by solutions with high total ion concentrations. The method was therefore unsuitable for the analysis of extracts from soil and plant materials prepared by wet ashing.

HPLC was used for the determination of nitrate and nitrite in environmental water samples[34]. The technique offered rapid analysis with minimal sample preparation, high sensitivity and few interferences. Samples were filtered prior to injection and eluted with the mobile phase, aqueous tetramethylammonium phosphate. The detection limit was calculated as 0.1mg 1^{-1} using an absorbance detector at 214nm.

Chromatographic methods have also been applied to the determination of nitrite and nitrate in human plasma[35]. Sample preparation involved the precipitation of plasma the supernatant was then injected onto a reverse phase precolumn. A poly(styrene-divinylbenzene) based ion-exchange column was used to separate the ions with U.V. detection at 214nm. Sensitivity of 0.01mM and linearity from 0.02-1.0mM were experienced for both ions. Few interferences were experienced because of the removal of proteins by precipitation, organic molecules by a reverse phase precolumn and good resolution of the peaks in the chromatogram.

The determination of nitrate and nitrite in meat products was also accomplished using HPLC[36]. The meat products were extracted, centrifuged and 20μl of the filtered supernatant was injected onto the column. The mobile phase was acetonitrile/tetrapentylammonium bromide; the column was packed with non-polar poly(styrene-divinylbenzene) and detection was spectrophotometric.

Reversed phase liquid chromatography was used for the separation of organic and inorganic anions[37]. The eluent contained the octylamine salt of a mineral acid which separated inorganic anions such as bromide, iodide, nitrite, iodate and cyanate. The method was used for waste-waters and silage. Conventional liquid chromatography apparatus was used with a U.V. detector at 205nm. The inorganic ions showed linear response in the concentration range 1-2500ppm.

Alawi[38] used HPLC for the determination of nitrate and nitrite in water at a level of 5ng ml^{-1}(ppb). The method was indirect in comparison to the HPLC methods previously described. It was based on the nitration of an excess of phenol; the O-nitrophenol was extracted and separated using a reversed phase column, and detected amperometrically in the reduction mode.

Gas-liquid chromatography (G.L.C.) was used for the analysis of meat products and cheeses[39]. The detection limit was 0.006μg ml^{-1} NO_3N and the range of determination 0.05-1.0μg. Nitrate was extracted from finely ground samples with hot sodium hydroxide solution. The solution was reacted with 2-sec-butylphenol in sulphuric acid to form the nitrated product, 4-nitro-2-sec-butylphenol, which was extracted with toluene. The toluene solution was re-extracted with an alkaline solution which was then analysed by G.L.C. with an electron capture detector. Interferences from nitrite

and chloride were controlled using sulphamic acid and sodium sulphate.

The use of chromatography for the determination of ions in environmental samples has a number of limitations. The equipment required for these analyses is expensive. Precautions must be taken when analysing real samples to prevent damage to the columns.

1.2.6 Miscellanous Methods

Methods for determining organic or inorganic nitrate in the presence of other ions were suggested by Hassan[40]. The methods were based on the reduction of nitrate with cadmium metal and 0.1M hydrochloric acid. Four equivalents of cadmium ions were released per mole of nitrate and nitrite nitrogen, which was converted to nitrous oxide. Four methods for determining the cadmium ions were compared: atomic absorption spectrometry at 228.8nm; polarography; potentiometric EDTA titration at pH 10 with cadmium ISE, and EDTA titration with Erichrome Black T indicator. Organic nitrate was determined in the range 0.5-50μM without interference from common anions and cations, the method was accurate and precise.

The strong reducing agent chromium (II) was used in flow injection analysis of nitrate solutions.[41]

Although chromium (II) is unstable under atmospheric conditions only partial oxidation occurs in flow systems, the extent of oxidation is highly reproducible. Nitrate and nitrite were reduced to ammonia and a polarographic detector at a working potential of -1.5V was used to monitor the change in chromium (III)-EDTA concentration. Good linearity was obtained in sample solutions of 2.5×10^{-5}-10^{-4}M. The production of hydrazine or hydroxylamine by side reactions prevents the reaction with chromium (II)-EDTA and so causes reduced nitrate levels.

A complex voltammetric electrode was designed for the determination of nitrate[42]. An anion-exchange membrane was used to enclose a small volume electrolysis cell which included a constrained mercury column indicator electrode. Filter paper impregnated with 0.1M KCl and 0.01M $ZrOCl_2$ electrolyte as catalyst, served as a constraining barrier and spacer for the thin layer electrolysis chamber. Selective transfer of nitrate from the sample to the electrolysis chamber, through the ion-exchange membrane, occurred by Donnan dialysis. Controlled potential electrolysis at -1.25V vs Ag/AgCl electrode provided the sensing current, the value of which was proportional to the sample concentration of nitrate. The limit of detection using the current at 8min. was 6.7×10^{-6}M NO_3. The method was linear over

3 decades of concentration.

Nitrate was also determined voltammetrically by Fogg et al.[43] in a flow injection system. Reduction of nitrate was carried out on a batch basis with cadmium or online with cadmium wire. The nitrite produced was then injected into an acidic bromide eluent. The nitrite was monitored by the reduction signal at a glassy carbon electrode held at 0.3V.

1.2.7 Ion-Selective Electrode Methods

Unlike the previous methods ion-selective electrodes are suitable for the analysis of environmental samples without sample pretreatment. Ion-selective electrodes provide a fast, cheap and relatively versatile method for nitrate determination. Ion-selective electrodes measure the activity of a given ion in the presence of other ions, HPLC also measures the activity of an ion, other methods measure the ions concentration.

The present range of commercial I.S.E. suffer some interferences from common ions; but do not suffer interference from turbid samples. They are suitable for on-line continuous analysis. A standard method for nitrate determination with an I.S.E. exists[5]. Nitrate activity is measured potentiometrically in the treated sample by means of a nitrate selective electrode using a calibration curve or standard addition method. The standards are treated with a reagent to make their

ionic strength and pH value uniform. The range of application is 1-1000mg 1^{-1}; the limit of detection is 0.05 to 0.5mg 1^{-1}. Manual sample analysis time is approximately 15 minutes for electrode calibration and analysis of a single sample but 5 minutes for subsequent samples.

Nitrate electrodes suffer interference from several commonly occurring anions, selectivity coefficients depend upon the type of electrode. Chloride, carbonate and detergents are common interferents. Treatment with sulphamic acid may be required to remove high levels of nitrite. Many examples of nitrate analysis by I.S.E. are present in the literature. A brief discussion of a number of examples will be used to illustrate the versatility of this method.

Milham et al.[44] used an early commercial nitrate electrode (Orion Model 92-07)to analyse plant, soil and water samples. A specially prepared buffer solution was used to eliminate interferences from chloride, nitrite and organic anions. A linear calibration was obtained from 5-1000ppm. The limit of detection for water samples was 10ppm. The Orion 92-07 was also used to monitor the bacterial growth curves of E.coli.[45] The nitrate levels in the cell culture were monitored directly every 6 hours by inserting the electrodes. The electrodes were also used for the assay of nitrate reductase activity. The technique was found to be superior to spectrophotometric methods.

Hulanicki et al.[46] used a more advanced electrode to monitor nitrate in water. Phosphate buffer and silver sulphate were used to control interferences. The electrode was suitable for measurements down to 10^{-5}M; it was used for nitrate in tap-water at the level 8-10ppm.

A Corning nitrate electrode was used to measure nitrate in grass and clover.[47] Dried samples were mixed with buffered extraction solution and allowed to stand, the nitrate in the solution was then determined by direct measurement of the solution.

The simplicity of operation and portability of I.S.E. were illustrated by Bound who used a nitrate I.S.E. to monitor nitrate in soil pastes.[48] The method could be used in the field to provide a map of nutrient concentrations. The use of I.S.E. for monitoring nitrate in soils was also investigated by Black and Waring.[49] They used a K_2SO_4 solution to extract nitrate from adsorbing soils high in clay minerals. An aliquot of extractant was further diluted with K_2SO_4 and nitrate was determined by placing the I.S.E. in the solution. Sample readings were obtained in 15s for samples >1mg l^{-1} and 30-60s for lower concentrations. The calibration was linear between 0.5-20mg 1^{-1} NO_3.N.

The determination of nitrate in meat products was carried out using an Orion 93-07 I.S.E.[50] Homogenised samples of meat products were extracted with borax buffer (pH9). An aliquot of the extractant was then mixed with a specially prepared buffer solution which removed interfering ions, finally the pH was adjusted to 3.3. The method showed good precision and agreement with spectrophotometric methods; it showed linear response between 5.6×10^{-5} - 10^{-2}M of nitrate.

Ion-selective electrodes may be used to advantage in flowing streams where response and recovery times for the electrodes are enhanced. Flow Injection Analysis (F.I.A.) is a useful adaptation for many analytical procedures. A flowing stream is used to carry sample and reagents and time is allowed for reactions to occur before the stream passes through a detector. Sequential addition of reagents, stream splitting and multiple analysis may be incorporated into the system. Flowing systems are now used for the rapid processing of large numbers of samples by established methods.

Nitrate I.S.E. were used for the assay of nitrate and nitrite reductase activity in a flow-stream technique.[51] Ruzicka et al. used F.I.A. and I.S.E. to monitor soil extracts for nitrate.[52] The detection limit was 1×10^{-5}M for nitrate. Hansen et al.[53] used F.I.A. for the analysis of nitrate in environmental samples of waste-waters and soil extracts.

Nitrate in soil extracts was determined using a nitrate-selective flow electrode method[54] and compared with a reduction-distillation and a cadmium-reduction method. The range of application was 0.5-100μgml^{-1} NO_3.N; 20 samples per hour were processed. Equivalent results were obtained using all three methods.

Trojanowicz and Lewandowski[55] used a flow-through system for the continuous potentiometric determination of chloride, fluoride, nitrate and ammonia in natural waters. The method was used for samples in the range 5-20ppm nitrate.

1.3 Nitrate-Selective Electrodes

1.3.1 Principles of Ion-Selective Electrodes

Ion-selective electrodes are devices which enable the activity of a given ion, in a solution to be determined potentiometrically. They consist of a selective membrane, an internal reference electrolyte (filling solution) and an internal reference electrode, which form a half-cell. An external reference electrode completes the circuit. When the ion-selective membrane is immersed in a solution of ions a potential difference is generated between the internal filling solution and the sample solution, across the membrane. The potential (E) varies with ion activity according to the Nernst equation:

$$E = E^{\ominus} + \frac{RT}{zF} \log_e a_i$$

$E^{\ominus}$ = standard potential

R = gas constant

T = absolute temperature

z = charge on the ion

a_i = activity

When, as is customary, the relationship is expressed as millivolts per decade change in ion activity, ΔE is close to 60 $mV_{decade^{-1}}$ at $25^{o}C$ for monovalent ions - Nernstian response.

The membrane components of I.S.E. vary considerably and may be used to define the type of electrode. The development of I.S.E. is outlined below with particular emphasis on nitrate responsive electrodes.

1.3.2 The Earliest Electrodes

Until recent years ion-selective electrodes were limited to classical glass electrodes and certain solid state electrodes which contained non-porous membranes; usually a large crystal or a disc composed of electro-active material.

The solid state electrodes are somewhat limited because of the stringent requirements which the membrane material must satisfy. It must be highly insoluble, non-porous and have a sufficient mechanical strength. However, the most limiting requirement is the conductivity

of the membrane. The useful solid state electrodes in existence all exhibit abnormally high membrane conductivities.

The first electrode system responsive to anions was developed by Sollner[56], the membranes were produced by impregnating collodion with protamine. These membranes were electropositive and could be used to detect several anions. The electrodes were used mainly in electrometric titrations because they were sensitive but not selective.

A solid-state membrane electrode for nitrate was prepared from compressed silver diethyldithiocarbamate powder[57]. After conditioning in nitrate solution the electrode showed Nernstian response to nitrate in the range 10^{-1}-10^{-6}M of nitrate ion; the selectivity coefficient for nitrate over chloride ion was 3.0×10^{-2}.

1.3.3 Nitrate Electrodes with Liquid Membranes

The first ion-selective electrodes available commercially were of the liquid ion-exhanger type. These electrodes consisted of a porous membrane which supported a water immiscible solution of ion-exchanger and solvent. The first electrodes were prepared using an Orion 92-20 calcium electrode[58] by replacing the internal solutions with a suitable exchanger for nitrate. The original ion-exchanger used by Orion for nitrate, was a tris(substituted 1,10 phenanthroline)Ni(II) complex[59]. Later Orion and Beckman electrodes contained

tetra-alkylammonium cations. Corning used tridodecylhexadecylammonium nitrate in n-octyl-p-nitrophenyl ether[60]. The quaternary ammonium salt, methyl tricaprylyl ammonium nitrate in 1-decanol was used by Coetzee and Freiser[61.62]. A recent liquid membrane was constructed using a 4,4'-diphenyl-2,2'-bipyridine complex in 2-nitro-p-cymene[63].

This new type of electrode was a considerable improvement on the early protamine-collodion membranes and gave Nernstian response over a useful working range. However, these electrodes also showed poor sensitivity and gradual changes in both sensitivity and selectivity. The major drawback was the cumbersome construction of the electrodes. The porous membranes holding the water immiscible mixture of ion-exchanger and solvent allow constant leakage of the electroactive liquid to occur. The internal arrangement of the electrode required reservoirs for the exchanger which must be separated from the inner electrolyte. This lead to complicated electrode construction and difficulty when replenishing electrode components. A further complication was caused by pressure and temperature fluctuations which influence the barrier formed by the organic liquid in the membrane pores. These electrodes also showed poor resistance to pressure, which may make them unsuitable for use in continuous flow systems which undergo pressure fluctuations.

1.3.4 Polymer Membrane Electrodes

An important advance in I.S.E. technology was the introduction of non-porous poly(vinyl chloride) PVC membranes by Moody et al. in 1970[64]. Nitrate responsive membranes were produced[65] by adding Corning 477316 or Orion 92-07-02 nitrate liquid ion-exchangers to a solution of PVC in THF. The solvent was allowed to evaporate producing a solid membrane. The construction of electrodes was simplified and their lifetime improved by the use of these new membranes. The characteristics of these new membranes were dependent on the ion-exchanger. The PVC based membranes responded to nitrate in the concentration range 10^{-1}-10^{-4}M, the main interferent was iodide.

Nielsen and Hansen[66] used the new type of membrane and long-chain quaternary ammonium salts (QAS) to construct a sensitive nitrate electrode. Their choice of electroactive material was based on the solubility of the membrane components. The PVC electrodes are eseentially liquid exchange membranes, but the porous membrane was replaced by a solid polymer support in which the electrocative material is entangled. The performance of the electrode is dependant on the insolubility of the membrane materials in the test solutions. Nielsen and Hansen chose several Q.A.S. for examination as sensors: tetradodecylammonium nitrate, trioctylmethylammonium

nitrate, and tetraheptylammonium nitrate. The new electrodes were superior in stability and sensitivity to any previous electrodes, the limit of detection was approximately 7.9×10^{-7}M and the selectivity coefficient for nitrate over chloride was 5×10^{-3}. The new membrane, tetradodecylammonium nitrate, P.V.C. and dibutylphthalate plasticiser is used in several commercial electrodes.

The ion association complex of bis(neocuprione) copper (1) and nitrate was reported to show better selectivity towards iodide and sulphate than the Orion exchanger when used in a P.V.C. liquid membrane[67].

1.3.4.1 Coated-wire Electrodes

Coated-wire electrodes are a variation on the P.V.C. membrane electrode; the membrane is in direct contact with the internal reference. The construction of these electrodes is relatively simple as no internal filling solution is required. The electrodes are produced by repeated dipping of a prepared metal wire into a solution of polymer and ion-exchanger. A coated-wire electrode was developed using Aliquat 336S in poly (methyl methacrylate) on platinum wire[68]. Aliquat 336S (methyl tricaprylyl ammonium chloride) has been used in several liquid membrane electrodes.

Coated-wire electrodes often show unstable standard potentials. The electrochemical process at the metal-membrane interface is not fully understood. The effect of oxygen and the state of the platinum contact on the potential stability were investigated for the nitrate electrode[69]. The electrode studied was constructed from PVC and tris(bathophenanthroline) nickel(II)nitrate in 2-nitrophenyl phenyl ether.

1.3.4.2 Bound Ion-exchanger Electrodes

Polymer membrane electrodes are now well established in several areas of analytical chemistry. However, improvement in the properties of the membranes could extend their applications considerably. Poly (vinylchloride) PVC is a commonly used matrix material, but has poor mechanical qualities, and very little resistance to chemically hostile environments. Silicone rubbers exhibit superior resistance to hostile environments when crosslinked, but additional processing is then required. However, even if the matrix material is robust, the ion-exchanger is usually vulnerable to physical or chemical deterioration. A major weakness of entangled exchangers is the ease by which they can be removed from the polymer support by leaching. Covalent attachment of the ion-exchanger to the matrix material would improve the lifetime of the electrodes. Covalent attachment to a polymer matrix of suitable properties would improve the chemical resistance of the electrodes.

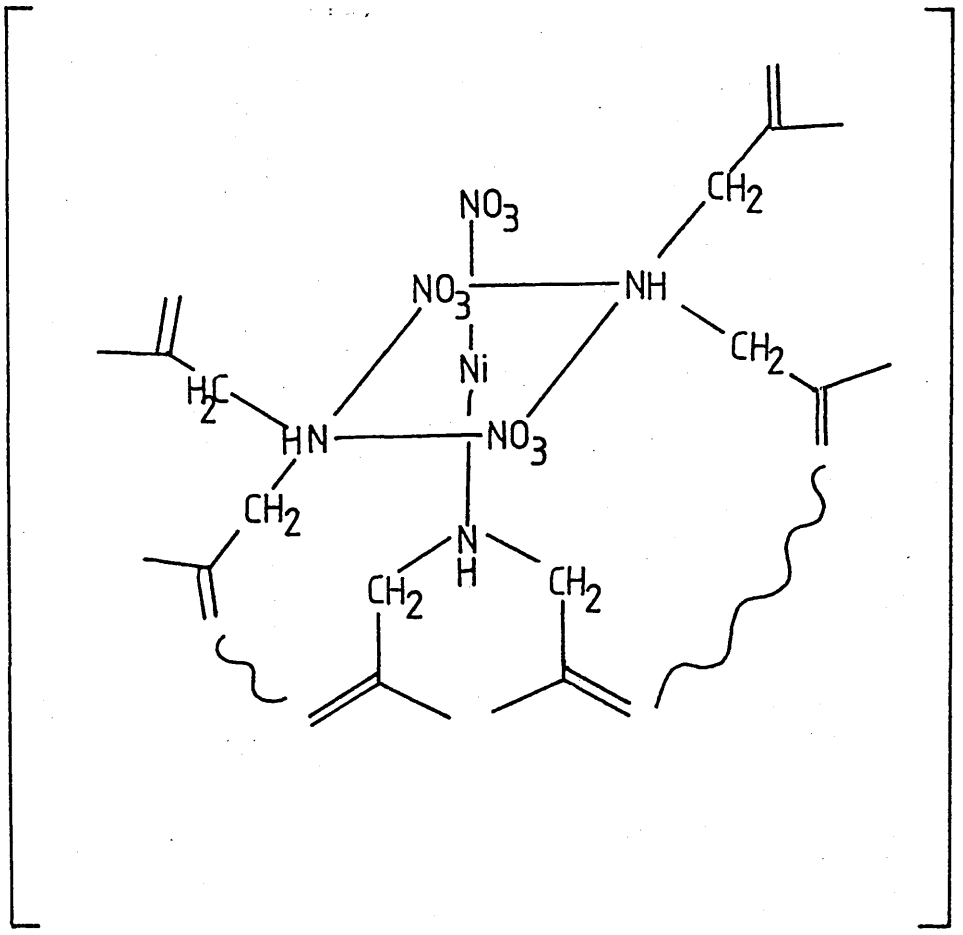


Fig.1.1 The nickel unit in Bakelite polymer.

A brief discussion of the different approaches to this problem is included below.

a) The Work of Dobblestein and Diehl

In the late 1960's Dobblestein and Diehl accidentally discovered a membrane system which was responsive to nitrate[70]. They were working on membranes impregnated with nickel dimethylglyoximate in order to produce an electrode for nickel. Problems of solubility caused them to try a solution of nickel 4,4' dihydroxybenzildioximate in Bakelite A polymer; this was polymerised to Bakelite C using ammonia as a catalyst. The idea behind the choice of reagent was to obtain an even dispersion throughout the membrane by involving the phenolic groups in the polymer.

The membranes were ordered crystalline materials. They responded to univalent anions and hydrogen. The structure was examined by X-ray powder diffraction and the role of each reagent was investigated. The structure (Figure 1.1) shows that the nickel is complexed by the polymeric framework. This is not a covalently bound sensor because like other complexes its stability depends on conditions and preferential complexation of other metal ions may occur changing the properties of the membrane.

b) The Work of Jyo

Jyo and coworkers developed a new type of anion-selective electrode[71]. The membrane was an anion-exchange resin impregnated with nitrobenzene and the exchange site was a hydrophobic quaternary ammonium group with a long alkyl chain.

This anion exchange resin was prepared by the chloromethylation of Amberlite, a cross-linked styrene-divinylbenzene copolymer, and the subsequent quaternisation of the chloromethylated resin with dimethyltetradecylamine. The membrane was then conditioned and impregnated with nitrobenzene. The lower limit of Nernstian response for this electrode was 10^{-3}-10^{-4}M.

A later membrane[72] was based on a homogeneous cross-linked polystyrene with covalently attached benzyltrioctylammonium ions. The membrane showed acceptable electroanalytical properties but was hard and mechanically weak. The preparation of the membrane was later modified to produce a more robust polymer[73]. An oleophilic anion exchange resin reinforced with polypropylene was prepared by cross-linking in a multistep reaction. The membrane was treated with chloromethane, quaternised with trioctylamine, and impregnated with nitrobenzene. The new membranes showed near Nernstian response to nitrate with a lower limit of response being 5×10^{-5}M and the selectivity coefficient

for nitrate over chloride was 7.9×10^{-3} in mixed solution.

c) Other Ideas

The production of polymers with covalently bound sensors was investigated by several groups of workers. These were systematic investigations of new materials, rather than adaptations of existing materials or accidental discoveries of materials with suitable properties.

Keil et al.[74] used a vinyl alcohol/vinyl chloride copolymer, alkyl phosphate groups were grafted to the polymer at the hydroxyl sites. The polymer was prepared for use in a calcium ion-selective electrode. The ion-selective polymer was then entangled in a poly(vinyl chloride) PVC support matrix and used in an ion-selective electrode. The electrode showed a fast and steady response to calcium but an improvement in lifetime was not observed.

Cationic surfactant[75] electrodes were made by sulphonating PVC during polymerisation to produce anionic groups in the polymer. Anionic surfactant[75] electrodes were prepared by chain termination of PVC with an amine, and quaternisation of the final polymeric material to produce positively charged sites. The lifetime of these surfactant electrodes was extended in comparison with liquid ion-exchanger surfactant electrodes - the lifetime was limited by the leaching of the plasticiser.

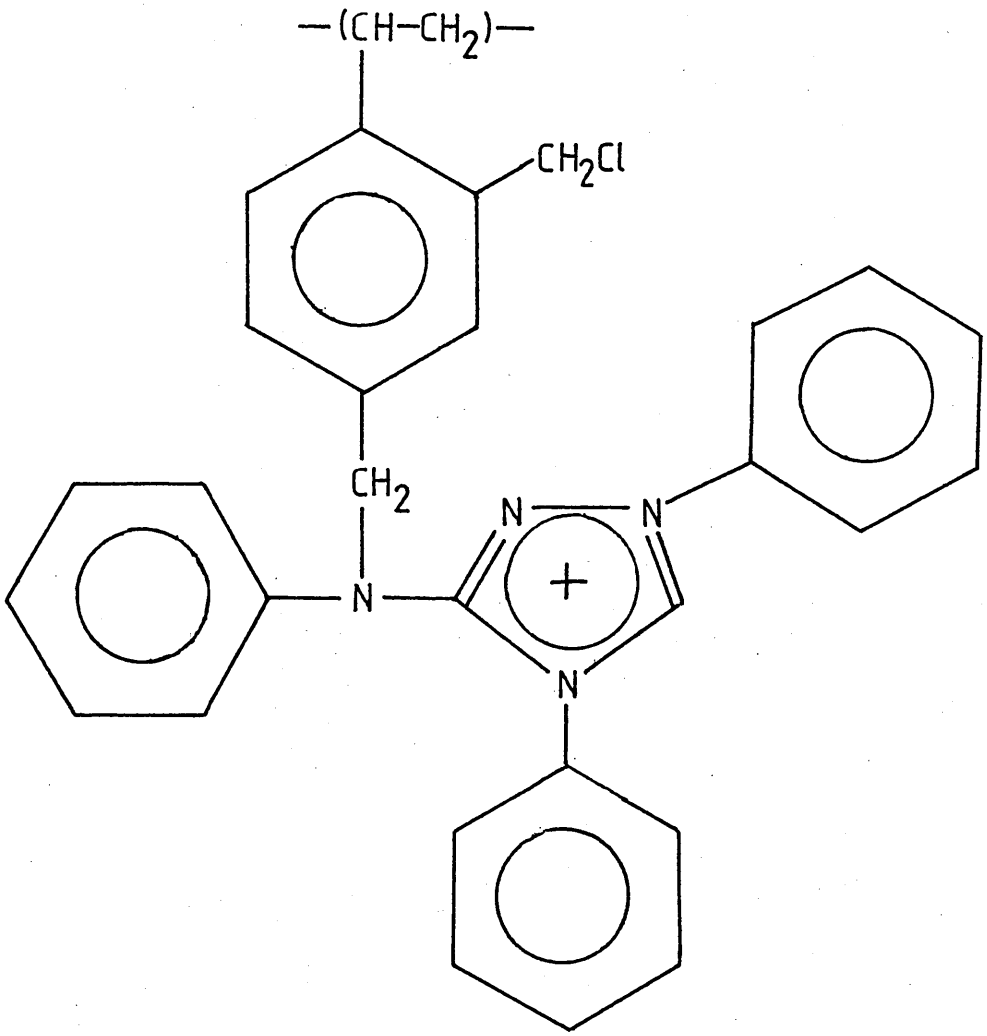


Fig. 1.2 1,4 diphenyl-3 ,-phenylimino-1,2,4 triazoline.

Chiou et al.[76] attempted to synthesise a nitrate selective polymer by incorporating a nitron group (1,4 diphenyl -3,-phenylimino-1,2,4 triazoline) (Figure 1.2) into the polymer backbone. The polymer was reported to have reasonable selectivity but low capacity as an ion-exchange resin. Increasing the number of nitron groups in the polymer backbone resulted in a reasonably selective polymer for the removal of oxidising anions such as NO_3^-, NO_2^-, ClO_4^-, ReO_4^-, TaO_4^-, MoO_4^{2-}, $Cr_2O_7^{2-}$, NO_4^{2-}, MnO_4^-. The resin was suitable for removing nitrate and nitrite from water supplies - these would be the only oxidising anions present in appreciable concentration. Regeneration of the resin was required after each ion-exchange process.

Lawton and Yacynych[77] described the preparation of graphite electrodes coated with modified polymers. Several polymers were used, including polymeric quaternary ammonium salts. The membranes were prepared from vinylbenzyl chloride monomer which after polymerisation was modified by nucleophilic substitution. The nitrate electrode was made from poly triethyl(vinylbenzyl) ammonium chloride . The polymer membranes are not cross-linked and dissolve in a number of organic solvents. The electrode showed sub-Nernstian response to nitrate in the range 1×10^{-2} - 1×10^{-5}M.

In an earlier research project[78] in this laboratory, an ion-selective electrode for calcium was prepared which had a superior lifetime, compared to PVC membranes, and was capable of operating in hostile environments. The selective membrane was prepared using triallylphosphate groups as sensors, and a robust polymer, styrene-butadiene-styrene. The phosphate groups were covalently attached to the cross-linked polymer.

1.3.5 Aims of this Work

The essential requirements for ion-selective electrodes are outlined below. They should:

(i) be of simple construction and easy to handle;

(ii) be easy to calibrate and give reproducible and meaningful results within the everyday range of ion activities 10^{-2} - 10^{-5}M;

(iii) have a fast response time so that a constant e.m.f. is attained within minutes at most;

(iv) have little or no memory effect, in order to allow vastly different analyte solutions to be measured rapidly (essential for on-line applications);

(v) be highly selective, that is measure the correct activities of the ion of interest irrespective of the presence of other ions - interference should be insignificant.

It is also useful if the electrode shows Nerstian response over the normal working range, but it is not essential. The electrode should also be robust allowing it to be used in hostile physical and chemical environments. It should also require little maintenance and have a lifetime of several months when in constant use.

The aim of this work was to develop a nitrate-selective electrode with a covalently bound sensor group. Such an electrode would be expected to have an improved lifetime compared to liquid and polymer entangled electrodes because the electroactive material would not leach from the membrane.

CHAPTER 2

CHOICE AND PREPARATION OF MATERIALS AND PRODUCTION OF MEMBRANES

2.1 The Polymer

The introduction of polymers as support materials for ion-selective membranes was a significant advance in electrode technology, simplifying construction and improving lifetimes. The majority of commercial, polymer membranes are made from poly(vinyl chloride) PVC. However this polymer has several limitations. Hostile chemical environments cause poor response and accelerate the deterioration of the membrane[79]. PVC requires a plasticiser to lower the glass transition temperature of the polymer and facilitate charge transport. Unplasticised PVC is a hard resilient material, suited to use in the construction industry. Polymer membranes may contain as much as 70% W/W of plasticiser, such membranes are soft, gelatinous and prone to distortion by pressure. The shelf life of a PVC electrode is affected by the presence of a plasticiser. Slow evaporation of the plasticiser may occur causing the membrane to harden and the response of the electrode to deteriorate.

A number of other polymers have been examined for their suitability as polymer membranes for ion-selective electrodes. Poly(vinyl isobutyl ether) was used to prepare a calcium selective membrane[80]. The polymer was not expected to require a plasticiser because the presence of bulky isobutyl groups produced a low glass transition temperature. However the polymer membranes showed good response only when the sensor material had plasticising properties. Silicone rubber was used as a matrix material for a potassium electrode[81], the sensor valinomycin was entangled in the cross-linked rubber matrix. The electrode operated successfully without a plasticiser. A potassium electrode with a long lifetime[82] was prepared from the block copolymer poly(bisphenol - A carbonate) and poly(dimethylsiloxane) with valinomycin as the sensor. The block copolymer was a two phase system; the polysiloxane blocks formed a continuous amorphous phase through which molecular transport occurred, and the polycarbonate blocks formed a discontinuous crystalline phase cross-linking the structure.

The entanglement of the sensor material in a robust cross-linked polymer such as silicone rubber would improve the physical properties of the membranes, and their resistance to hostile environments. However the limiting factor in the lifetime of an electrode membrane, is the rate at which the electroactive material is

leached from the supporting polymer. The leaching of electroactive material is accelerated when an electrode is used for continuous monitoring in a flowing stream of analyte. Covalent attachment of the electroactive material to an improved polymer matrix would prevent it leaching from the membrane.

These specifications resulted in the choice of a triblock elastomer poly(styrene-b-butadiene-b-styrene) SBS, as a suitable matrix polymer for this work. The polymer was used previously by this group[78] in the preparation of a novel electrode. Triallylphosphate groups were covalently attached to the polymer membrane to produce a calcium electrode. The polymer SBS has the required physical and mechanical properties, it is easy to work with, well documented and readily available. The polymer becomes cross-linked via the butadiene unsaturation, to form an insoluble, tough polymer. The cross-linking reaction may be used to incorporate other units into the polymer by graft copolymerisation.

Several methods for attaching sensor groups to supporting polymers were discussed in Section 1.3.4.2. Cutler et al.[75] used a sensor which acted as a chain terminator in the polymerisation of the support polymer. The production of useful polymers by this method requires the manipulation and careful control of the polymerisation reaction. Jyo and coworkers[71,72,73]

modified existing polymers by chemical reaction at suitable sites, to form sensor groups. Polymers which have the required chemical characteristics for Jyo's method may not have the required physical properties. The method pioneered in this group[79] incorporates covalent attachment of the sensor and the cross-linking reactions of the polymer, in one step.

2.2 The Sensor

Nitrate selective electrodes usually contain a quaternary ammonium salt or tris(substituted-o phenanthroline)nickel(II) as the electrocative material.

Dobblestein and Diehl[70] produced a polymeric nickel complex using Bakelite polymer. Ikeda and Hamato[83] prepared poly(p-chlorostyrene) supported phenyl(dipyridyl)nickel chloride for use as a catalyst in polymerisation reactions. However, such nickel complexes do not yield covalently bound sensors, because only the ligands are covalently attached to the polymer. The nickel ion is essential to the action of the sensor, but under suitable conditions the nickel ions could be replaced by other metal ions. Displacement of the nickel ions may result in loss of response for nitrate.

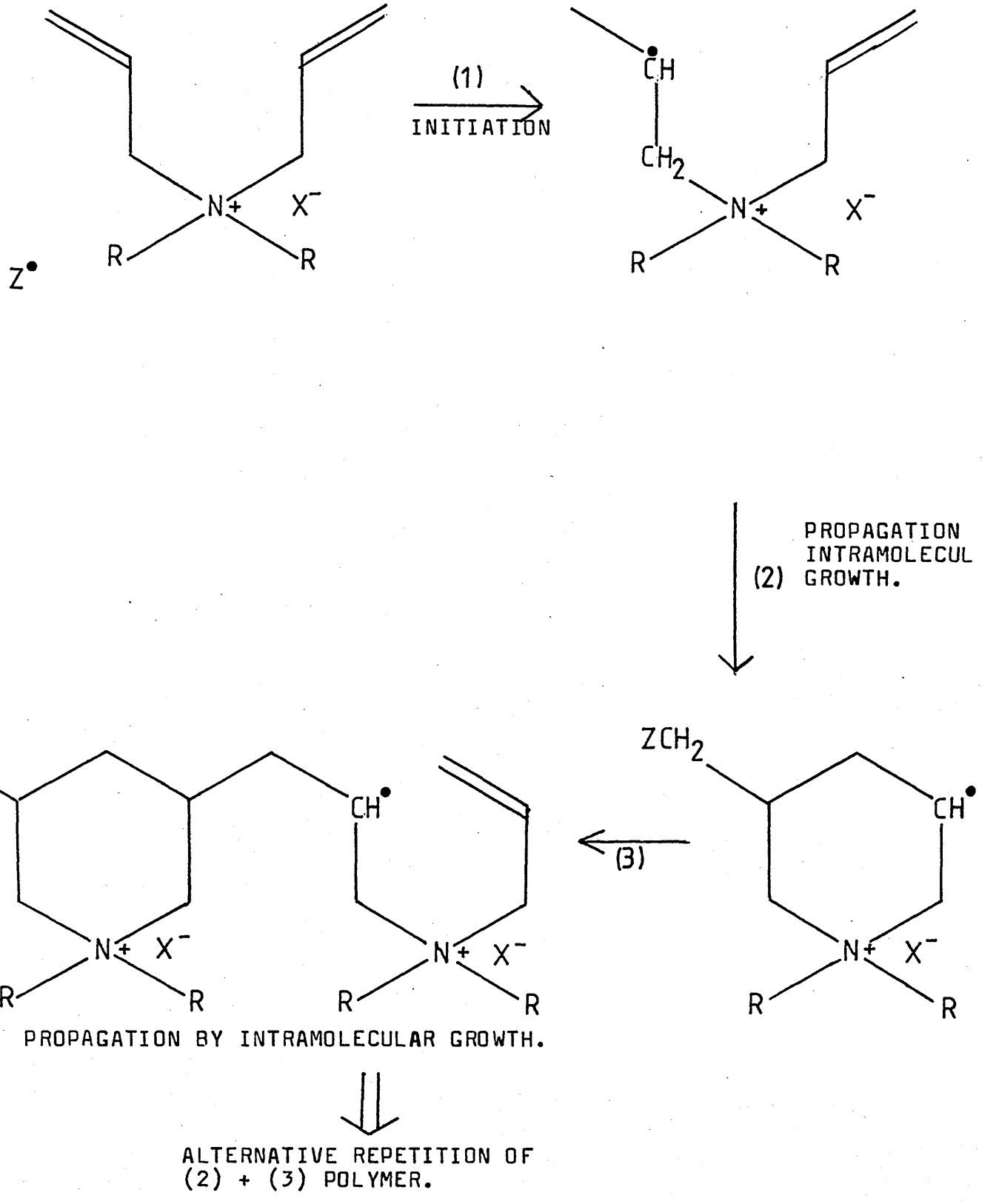


Fig.2.1 Proposed mechanism for polymerisation of diallyldialkylammonium halides.

Quaternary ammonium salts were chosen for this work because they will yield a true covalently bound system. In the late 1950's and early 1960's Butler et al. published a series of papers[84-92], on the synthesis and polymerisation of quaternary ammonium salts. The quaternary ammonium salts contained unsaturated groups such as allyl, dichloropropene, vinyloxyethyl or propargyl and formed linear or cross-linked polymers. The polymers were suitable for use as ion-exchange resins, but had very poor mechanical properties because of their low molecular weight. Quaternary ammonium salts with two unsaturated groups produced linear polymers which were water soluble. If the quaternary ammonium salt contained three or four unsaturated groups, water insoluble polymers were produced by cross-linking of polymer chains in a three dimensional network.

The polymerisation of these quaternary ammonium salts was attributed to a chain propagation mechanism which involved alternate intramolecular-intermolecular growth steps[92]. The proposed polymer structure was a linear chain of recurring n-substituted piperidinium halide units alternating along the chain with methylene groups, Figure 2.1. Later work has shown that the polymer consists of both five and six membered rings[93].

The structure and properties of these quaternary ammonium salts makes them suitable for covalent bonding to the SBS framework by radical initiation. The polymerisation and cyclopolymerisation properties of these quaternary ammonium salts are beyond the requirements of this project because we wish to attach relatively isolated quaternary nitrogens to the backbone of another polymer. However their susceptibility to radical initiation without breakdown of the quaternary structure is an extremely valuable property.

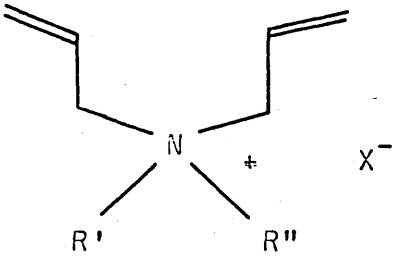
The quaternary ammonium salts of interest are white crystalline solids of a very hygroscopic nature. The intermediate tertiary amines are clear colourless liquids which would be easier to work with, but do not undergo polymerisation. The polymerisation reaction is only achieved if a quaternary nitrogen is present; tertiary amines act as radical scavengers, quenching polymerisation reactions.

Nielsen and Hansen[66] showed that quaternary ammonium salts with long alkyl chains improved the sensitivity of nitrate electrodes. These electrodes, mentioned earlier in Section 1.3.4., were of the PVC membrane type, with an entangled exchanger. The influence of the solubility coefficient of the QAS on the sensitivity of nitrate ISE was examined. Quaternary ammonium salts with long alkyl chains were less soluble

in water and leached more slowly from the membrane. The sensitivity is influenced by leaching because a point is reached when the amount of material being leached from the membrane into a dilute solution influences the response of the electrode. The long-term affect of leaching is to deplete the membrane of electroactive material causing a steady deterioration in the electrodes response. If the electroactive material is covalently bound to the polymer, its solubility coefficient will not influence the sensitivity of the electrode.

Nielsen and Hansen[66] also correlated increasing selectivity for nitrate with increasing chain length of the alkyl substituents, but the relationship was not illustrated by examples.

The quaternary ammonium salts selected for initial investigation in this work were diallyldialkylammonium chlorides;



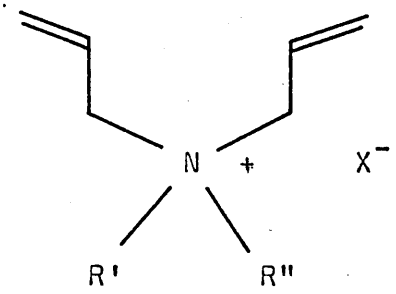
R'=R"=ethyl,butyl, hexyl, octyl

A range of quaternary ammonium salts was chosen in order to investigate the influence of the structures on electrode selectivity. The length of the alkyl substituents will be influenced by the covalent attachment of the quaternary nitrogen to a polymer network, which will provide substituents of infinite length. The chlorides were chosen because they are more susceptible to polymerisation than the bromides or iodides. Negi, Harada and Ishizuka[94] attributed this to the ease of oxidation of the halides which decreases $I^- < Br^- < Cl^-$. Therefore bromide ions are more easily oxidised than chloride, generating bromine which acts as an inhibitor to polymerisation by consumption of starting radicals and termination of growing chains.

2.2.1 Preparation of Quaternary Ammonium Salts

Butler's work[84-92] covered the preparation of a number of allyl substituted quaternary ammonium salts, but the diallyldihexylammonium and diallyldioctylammonium derivatives were not included. The preparation of tertiary amines and crystalline quaternary ammonium salts involved one or two step reactions, and should be applicable to a wide range of derivatives.

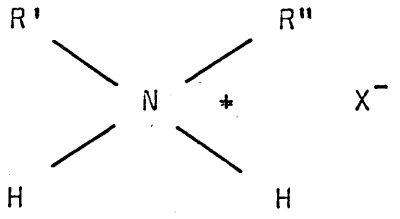
The synthesis of a wide range of polymerisable quaternary ammonium salts was outlined by Schuller and Thomas[94] and included:-



$X^-=Cl^-$, Br^-
R' and R" = 1-18C

The preparative details are sparse, but it appears that the quaternary ammonium salts were not isolated as monomers, but prepared and polymerised in situ, as an aqueous solution. Little difficulty was envisaged in the preparation of the chosen quaternary ammonium salts because of the extensive documentation of this class of compounds. In this work diallyldiethylammonium bromide and chloride were prepared using published methods[95], but these methods were unsuccessful for the synthesis of the butyl, hexyl and octyl derivatives. Many attempts were made to quaternise tertiary dialkylallyl-amines under different conditions. In most preparations an orange oil was produced, however under certain conditions (no solvent, ice cooled) a white solid was obtained. Unlike the diallyldiethylammonium halides, these solids were not hygroscopic and had a granular appearance. The dibutyl and dihexyl derivatives were water soluble. The dioctyl derivative was insoluble in water. The infrared spectra of these precipitates showed that the structures contained no allyl substituents. The n.m.r. spectra showed signals for the two alkyl groups attached to nitrogen, but no other signals. The white precipitates

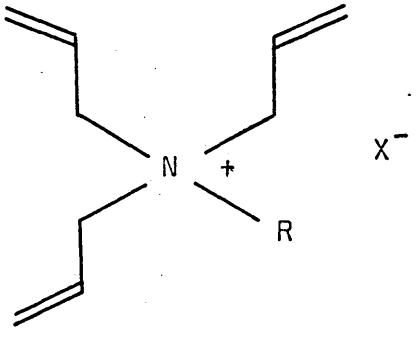
were considered to be secondary amine salts.



R' = R" = butyl, hexyl, octyl

This structure is consistent with the infrared and n.m.r. data. The absence of n.m.r. signals for the protons is probably due to exchange with D_2O solvent. Molecular models of diallyldialkylammonium salts indicate steric crowding of the substituents. This crowding may cause instability (in salts containing bulky alkyl groups), leading to loss of the allyl groups on quaternisation.

The following quaternary ammonium salts were made by quaternising an alkyldiallyamine with allyl bromide which is more reactive than allyl chloride



R= methyl
ethyl
propyl
butyl
allyl

The triallylalkylammonium salts appear to be less sterically crowded, less hygroscopic and easier to handle than the diallyl derivatives. The homologous series was not extended beyond butyl.

Triallylisopropylammonium bromide was also prepared but was susceptible to decomposition. The n.m.r. and infra-red spectra of triallylisopropylammonium bromide showed the presence of some allyl character, but some secondary ammonium salt was also present. Further recrystallisation increased decomposition. Decomposition of this quaternary ammonium salt may also be influenced by steric considerations because the isopropyl group is bulky compared to the other alkyl substituents.

2.2.2 Experimental Methods

The quaternary ammonium salts were prepared from suitable tertiary amines, the tertiary amines were prepared from commercially available primary or secondary amines.

2.2.2.1 Tertiary Amines

a) Allyldialkylamines

The preparation of allyldiethylamine will illustrate the procedure.

A secondary amine (diethylamine, 26g) was placed in a 3-necked flask with 25 cm^3 of distilled water. Then allyl chloride (26.20g) and sodium hydroxide solution (25-50cm^3; 14g of sodium hydroxide) were added dropwise, separately, from two funnels, with stirring. After the addition was complete the mixture was heated for 3-5 hours between 60-80^oC with stirring. After cooling the oily layer was separated, dried overnight using sodium hydroxide pellets and distilled using a fractionating side arm (the higher amines required vacuum distillation).

This method was used to prepare allyldiethylamine, allyldibutylamine, allyldihexylamine and allyldioctylamine. All were clear, colourless liquids. They were characterised by n.m.r. and ir. spectroscopy.

b) Diallylalkylamines

The preparation of diallylethylamine will illustrate the procedure.

Diallylamine (25g) was placed in a 3-necked flask with 25cm^3 of distilled water. Bromoethane (28g) was added dropwise, and then sodium hydroxide solution (25-50cm^3, 10-30g of sodium hydroxide) was also added dropwise with stirring. After the addition was complete the mixture was heated for 3-5 hours between 60-80^oC with stirring. The oily layer was treated as above.

This method was used for the preparation of diallylethylamine, diallylbutylamine, diallylhexylamine and diallyloctylamine. These were all clear colourless liquids.

2.2.2.2 Quaternisation

The quaternary ammonium salts of allylamines are extremely hygroscopic. Allyl chloride, allyl bromide, acetone and the tertiary amines were all dried and distilled immediately before reaction.

2.2.2.3 Diallyldiethylammonium Chloride

Allyl tertiary amine, was mixed with the equivalent amount of freshly distilled allylchloride in dry acetone. The white crystalline solid of quaternary ammonium salt gradually precipitated from the solution at room temperature. The solution was allowed to stand for a minimum of two days, and the liquor was then decanted. The crystals were repeatedly washed with cold acetone and dried by vacuum. The crystals were not collected by filtration because of their hygroscopic nature. This method proved unsuccessful for other quaternary ammonium salts.

2.2.2.4 Diallyldiethylammonium Bromide

Allyl bromide was added dropwise to the teriary amine in acetone. The mixture was stirred and the apparatus protected by a drying tube. It was necessary

to cool the reaction vessel in ice because of the exothermic nature of the reaction. The quaternary ammonium salt precipitated rapidly, and was collected by filtration, washed and dried under vacuum. Portions were recrystallied from hot acetone containing small quantities of absolute ethanol.

Several variations on these methods have been tried in order to prepare other quaternary ammonium salts. These include: gentle refluxing of the reaction mixture after addition of reagents; the use of different solvents (THF, acetophenone); or cooling of reaction vessel. In the majority of preparations no precipitate was observed and decomposition of either allylbromide or the tertiary amine began to occur.

White precipitates were collected from the reactions of the tertiary amines with allyl bromide in the absence of a solvent. These precipitates were recrystallised and examined. There was no evidence of allyl groups in either ir or nmr spectra of the products.

2.2.2.5 Triallylbutylammonium Bromide

Allyl bromide (4.84g) was added dropwise to a stirred solution of diallylbutylamine (7.9g) in dry acetone ($5cm^3$) cooled in an ice-bath. A precipitate developed slowly over several days. The crystals were

Table 2.1

Boiling Points of Tertiary Amines and Melting Points of Quaternary Ammonium Salts.

Tertiary Amine	bp/°C observed (lit)	Quaternary Ammonium Bromide	mp/°C observed (li
Diallylmethyl	109	Triallylmethyl	89 (91
Diallylethyl	123 (130)	Triallylethyl	158 (159
Diallylpropyl	147	Triallylpropyl	205 -
Diallylisopropyl	145		
Diallylbutyl	170 (170)	Triallylbutyl	177 (175
Triallyl	149 (149.5)	Tetraallyl	181 (185
Allyldimethyl	62 (62-63)		
Allyldiethyl	111 (110)	Diallyldiethyl	148 (155
Allyldipropyl	153 (150)	Allyltriethyl[a]	214 (202

a decomposes at 200°C

collected by decantation, and washed with dry THF to remove the orange oil from which they had precipitated, then recrystallied from hot acetone and absolute ethanol (9+1).

This method was also used to prepare triallymethyl-ammonium bromide, triallylethylammonium bromide and triallylpropylammonium bromide. Tetraallylammonium bromide was prepared from triallyamine and quaternised with allyl bromide.

2.2.2.6 Allyltriethylammonium Bromide

This quaternary ammonium salt was prepared by quaternisation of triethylamine with allyl bromide in dry acetone. The quaternary ammonium salt was chosen to complete the range of allyl substituted quaternary ammonium salts. The same material was also purchased from Lancaster Synthesis Ltd.

2.2.3 Characterisation

The tertiary amines were clear, colourless liquids and the quaternary ammonium salts were white or colourless crystals. The boiling points of the amines and melting points of the quarternary ammonium salts are given in Table 2.1. The characteristic ir and nmr spectral data for the triallyl homologous series is illustrated by the butyl derivatives (Tables 2.2 and 2.3). The ir and

Table 2.2

Infrared Spectral Characteristics of Amines and Salts

Sample	Sampling Method	Band/cm^{-1}	Interference
Diallylbutylamine	liquid film	1642	C=C allyl
		1000))) 920)	characteristic of allyl
Triallylbutyl ammonium bromide	KBr disc	1642	C=C allyl

Table 2.3

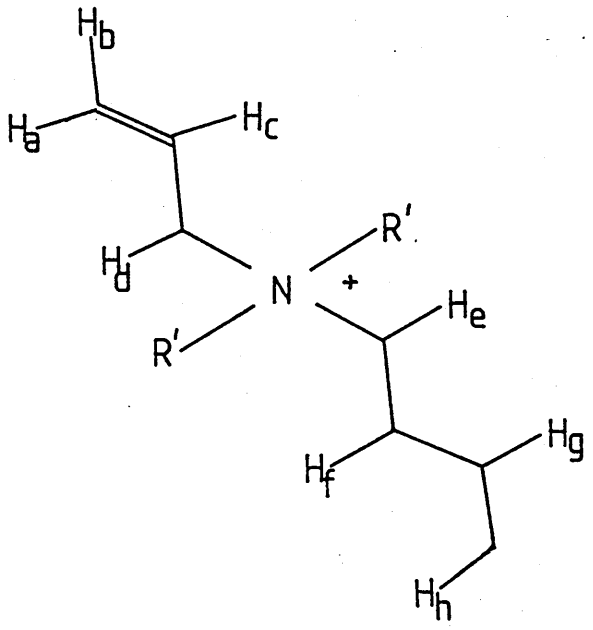
Characteristics of Triallylbutylammonium Bromide

^{1}H N.m.r.

δ/ppm[a]	H atom	relative intensity
6.05	H_c	3
5.70	H_a H_b	6
3.90 d	H_d	6
3.20 t	H_e	2
1.80	H_f	2
1.40	H_g	2
0.95 t	H_h	3

a Solvent D_2O

R'=allyl



Triallylbutylammonium Bromide

Table 2.4

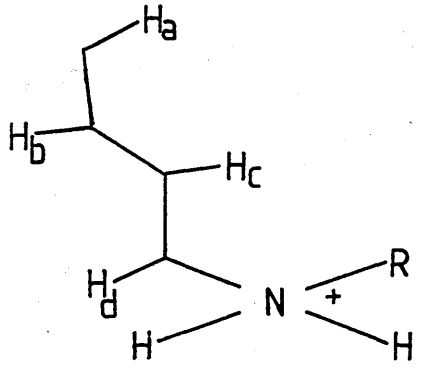
Infra-red and N.m.r. Spectral Characteristics of Decomposition Product

Infra-red band/cm^{-1}	Inference	
1600	secondary amine salt	NH_2^+
2500	gp. of signals secondary amine salt	NH_2^+

N.m.r.[a]

δ/ppm	H atom	relative intensity
2.70 t	H_a	4
1.30 q	H_b	4
1.05 m	H_c	4
0.60 t	H_d	6

a Solvent D_2O



R=butyl

Decomposition product of allyldibutylamine quaternised with allylbromide.

and nmr spectral data of the decomposition product, a secondary amine salt, do not exhibit allyl signals (Table 2.4).

2.3 Production of Membranes

The starting materials for this new type of ion-selective membrane were chosen for their suitability to a one-step copolymerisation reaction. An initiator is required to start chain growth reactions in the polymer, which will result in cross-linking and covalent attachment of the quaternary nitrogens. The azo-nitrile 2,2 azobis(2-methylproprionitrile) ABIN was used in the production of membranes with covalently bound sensors for calcium[78]. Radicals were generated by thermal or photochemical rupture of aliphatic azo-nitriles. Butler and co-workers[84] used the initiator tert-butylhydroperoxide (tBHP) to polymerise allyl substituted quaternary ammonium salts. This peroxide initiator forms radicals by thermal decomposition from 35-80^{o}C.

In order to produce a homogeneous polymer, a mixture or solution of the starting materials is required. The organic solvent tetrahydrofuran (THF) is a good solvent for SBS and was a suitable medium for free radical formation. The quaternary ammonium salts of interest were insoluble in THF but were soluble in

water and methanol.

The quaternary ammonium salts were prepared as either the chloride or bromide; the nitrate form of the salt is required for the electrode. The quaternary ammonium salts were used in the original form because of their hygroscopic nature. Conversion to the nitrate form by ion-exchange would have made recovery of the crystalline material difficult. The reactivity of these unsaturated ammonium compounds is related to their counter-ion, the reactivity of nitrates is unknown. Thus the quaternary ammonium halides were used for the preparation of membranes, and the halides will be replaced by nitrate by ion-exchange when the sensor is covalently attached to the polymer.

2.3.1 Preparation of Reagents

2.3.1.1 Poly(styrene-b-butadiene-b-styrene)SBS

The material used was the triblock elastomer, Cariflex Styrene Butadiene Rubber, supplied by Shell Chemicals, London. Several types of SBS are available with different proportions of styrene and butadiene. SBS.TR 1101 and TR 1102 were used for this project.

	% Butadiene	% Styrene	
1101	70	30	Higher Molecular Weight.Polymer
1102	72	28	Lower Molecular Weight. Polymer.

It was necessary to remove stabilisers which retard the proposed free-radical reaction. The polymer was dissolved in THF (24 hours) and precipitated into rapidly stirred, ice-cooled methanol. The resulting white precipitate was filtered and dried under vacuum. It was stored in a dark glass container in the refrigerator.

2.3.1.2 2,2 azobis(2-methylproprionitrile)(ABIN)

The initiator was supplied by Aldrich Chemicals. (Gillingham, Dorset). It was recrystallised from hot methanol. The resulting white, needle-like crystals were stored in the refrigerator.

2.3.1.3 tert-Butylhydroperoxide (tBHP)

Used as supplied by Koch-Light Laboratories, Ltd. (Colbrook, Berkshire). (70% + 30% di-tert-butylperoxide).

2.3.1.4 Tetrahydrofuran (THF)

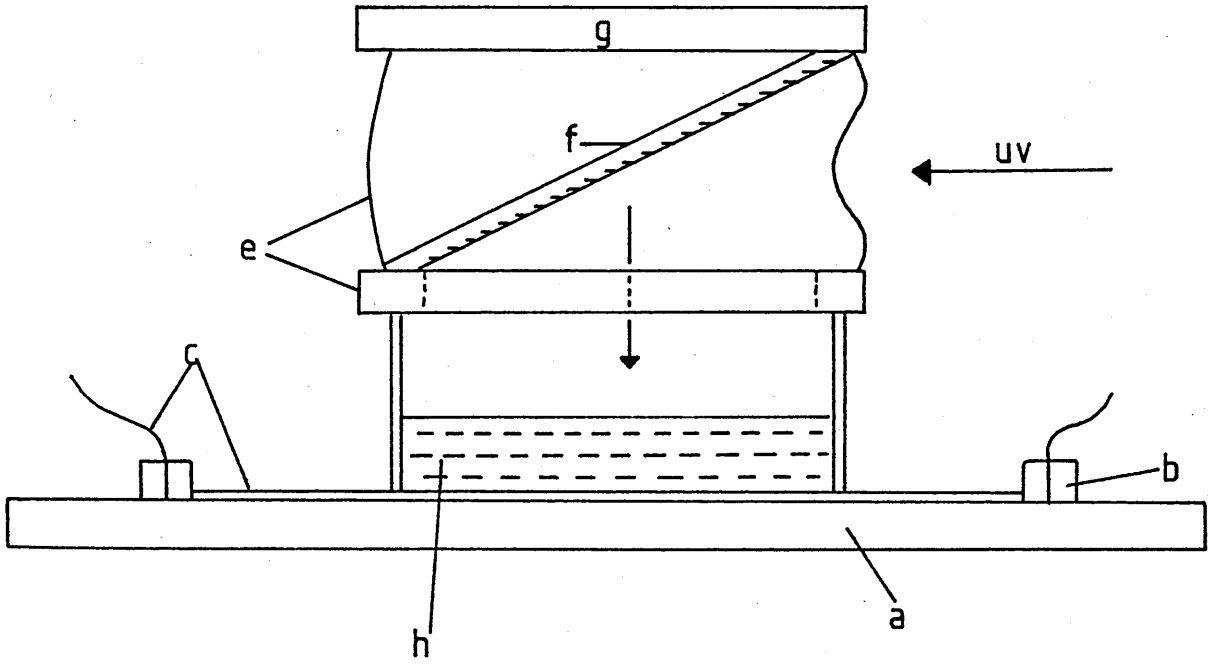
Tetrahydrofuran (puriss.p.a. Fluka, Fluorochem. Ltd., Glossop, Derbyshire) was refluxed over potassium metal for several hours and distilled. It was collected in a dark glass container and used immediately.

2.3.1.5 Methanol

Used as supplied by Aldrich Chemicals (Gillingham, Dorset). Spectrophotometric grade (Gold Label 99.9% pure).

2.3.1.6. Quaternary Ammonium Salts

The crystals were dried and stored in a vacuum dessicator.



a. glass plate

b. embroidery ring

c. cellophane film

d. glass ring (95 mm i.d.)

e. weight/mirror support

f. front-silvered mirror

g. weight

h. casting polymer soluti

Fig.2.2 Casting Apparatus

2.3.2 Methods of Membrane Preparation

Several methods for the preparation of cross-linked membranes with covalently bound sensors were evaluated.

2.3.2.1 Solvent Casting

The first method of membrane preparation to be evaluated was solvent casting. This method was used by Moody *et al.*[64] to produce PVC membranes, for ion-selective electrodes. The method was adopted for this work because it is effective and requires very little specialised equipment. The casting apparatus is illustrated in Figure 2.2. In order to cast a homogeneous membrane a solution or suspension of all the membrane components was required. The polymer and QAS solutions were found to be incompatible. The SBS polymer was dissolved in THF solvent, the QAS in methanol, but methanol caused the precipitation of the polymer from solution. In order to obtain a homogeneous solution the methanol/quaternary ammonium salt solution was made with the minimum amount of solvent and added dropwise to the SBS/THF solution, which was stirred rapidly for several minutes. In most membrane preparations a clear solution was obtained. Occasionally, with high levels of quaternary ammonium salts and therefore methanol, a colloidal suspension was obtained.

a) Method of Membrane preparation by Solvent Casting

Styrene-b-butadiene-b-styrene (SBS) (2g-4g) was dispersed in a suitable amount of freshly distilled THF (4g to 50 cm^3). The flask was sealed, flushed with argon or nitrogen and stored at sub-zero temperatures, in darkness for 24 hours, to allow the SBS to dissolve. The casting solution was prepared by adding the required amount of initiator (ABIN) and monomer (QAS) dissolved in THF and methanol respectively, to the flask. The solution was stirred for approximately 15 minutes and then poured into the casting apparatus.

The solution was contained in a 95mm i.d. glass ring supported by a pure cellophane film (W.E. Cannings Limited, Bristol), which was stretched between wooden embroidery rings to form a tight seal on the glass ring and prevent leakages (Figure 2.2).

Ultra-violet irradiation was used to photochemically decompose ABIN and release radicals in the solution. In order to direct the U.V. light onto the curing polymer a front silvered mirror was placed over the assembly. The U.V. source was an Osram ME/D medium pressure mercury discharge (Osram/GEC, London), which was situated between 0.5m and 1.0m from the glass ring.

The solution was irradiated overnight, approximately 15 hours. The membrane was then solid, and was removed from the apparatus, but not the glass ring. The cellophane was removed by peeling it from the membrane, it was

Table 2.5

Membranes prepared by U.V. Irradiation and Solvent Casting.

Code	SBS(g)	ABIN(g)	Monomer			
			Type	Amount(g)	%W/W[a]	
C1	4.00	0.1589	DADEAB	0.1322	3.31	
C2	4.00	0.0501	DADEAB	0.1339	3.35	
C3	4.00	0.1034	DADEAB	0.1318	3.30	Not Irradiated Not Cross-linke
D1	4.00	0.0843	DADEAB	0.1573	3.93	
D2	2.23	0.0406	"	-	-	
D3	4.03	0.0946	DADEAB	0.2066	5.13	
E1	4.00	0.0810	DADEAB	0.1620	4.05	
F1	4.00	0.0458	DADEAB	0.0877	2.19	
F2	2.75	0.0441	TAEAB	0.0795	2.89	
F3	2.59	0.0413	TAAB	0.0818	3.16	

DADEAB - Diallyldiethylammonium bromide a % W/W QAS/SBS

TAEAB - Triallylethylammonium bromide

TAAB - Tetraallylammonium bromide

sometimes necessary to moisten the cellophane before removing it. The membrane was then heated in a vacuum oven at 55°C to remove any traces of solvent.

Table 2.5 gives details of the master membranes, prepared by this method.

b) Modification of Casting Apparatus

The membranes produced in the single glass ring (95mm i.d.) were often uneven in texture and appearance. This was attributed in part to the different evaporation rates of the two solvents, methanol and THF. Evaporation of the solvents appears to have a chromatographic effect on the membrane components causing some areas to be cloudy or contain crystals, and others to be clear.

The original casting apparatus was modified by the use of three smaller glass rings (40 mm i.d.) in place of the single large ring. The smaller rings were individually sealed with cellophane and used in the weighted mirror arrangement Plate 2.1. The membranes produced using this apparatus were more even in appearance (Table 2.6 and 2.7).

The master membrane M6 produced a number of promising electrodes. Table 2.7 lists several membranes produced as variations of the M6 formulation by varying the amount of monomer but maintaining the amounts of

LATE 2.1

HE NEW CASTING APPARATUS

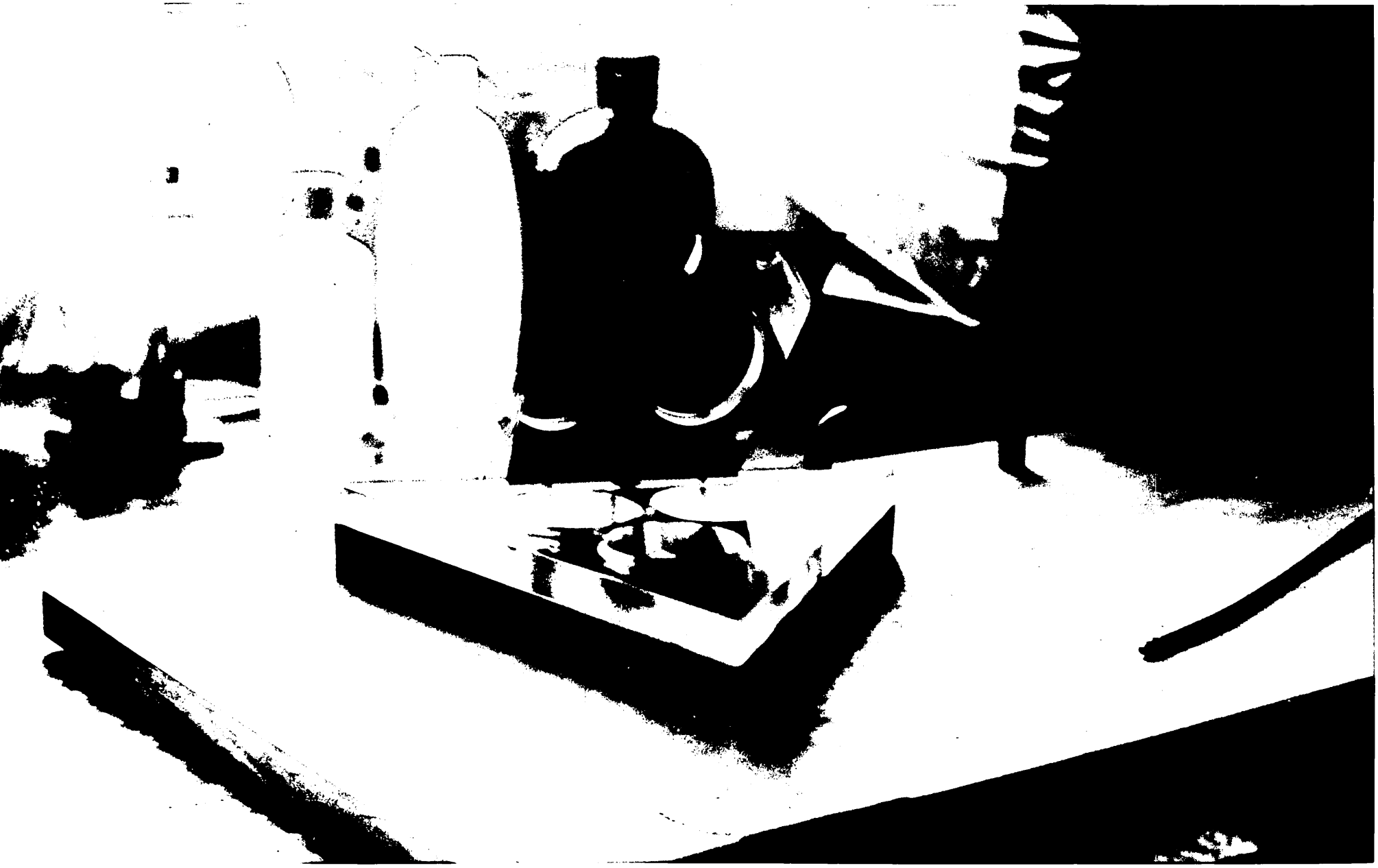


Table 2.6

Membranes Prepared with Increased QAS.

Code	SBS(g)	ABIN(g)	Monomer		% W/W[a]
			Type	Amount(g)	
1	2.5	0.1364	DADEAB	0.2706	10.82
2	2.47	0.1125	DADEAB	0.1683	6.81
3	2.48	0.2114	DADEAB	0.3018	12.17
5	2.51	0.1115	TABAB	0.1900	7.57
6	2.50	0.0694	TABAB	0.1957	7.83
7	2.00	0.0636	TABAB	0.1028	5.14
8	2.03	0.0757	TABAB	0.2184	10.76
9	2.02	0.0695	TAEAB	0.1633	8.08
MIJAN	2.01	0.0680	TAPAB	0.1609	8.00

a. % W/W QAS/SBS

DADEAB - Diallyldiethylammonium bromide

TABAB - Triallylbutylammonium bromide

TAEAB - Trialyethylammonium bromide

TAPAB - Triallylpropylammonium bromide

Table 2.7

Variations on Master Membrane M6

Code	SBS(g)	ABIN(g)	Monomer Type	Monomer Amount(g)	% W/W[a]
M6	2.50	0.0694	TABAB	0.1957	7.83
MFEB1	2.50	0.0708	TABAB	0.1992	7.97
MFEB3	2.50	0.0699	TABAB	0.2007	8.03
MFEB4	2.50	0.0694	TABAB	0.2351	9.40
MFEB5	2.51	0.0691	TABAB	0.2547	10.15

a % W/W QAS/SBS

TABAB - Triallylbutylammonium bromide

initiator and SBS constant.

2.3.2.2 Hot Pressing

The electroanalytical properties of the solvent cast membranes were encouraging but the response at low concentrations of nitrate was poor. Increased amounts of quaternary ammonium salt were incorporated into the membranes in order to produce a more sensitive electrode. The insolubility of the quaternary ammonium salts in THF caused some problems. As the amount of quaternary ammonium salt increased the homogeniety of the polymer membranes deteriorated. An alternative method of membrane fabrication was sought to overcome the solubility problems incurred by solvent casting methods.

A common method for processing polymeric material into useful forms is hot pressing. The polymer is hydraulically compressed at a temperature which induces it to flow and it can then be moulded into the desired physical form. Cross-linking is thermally initiated in the SBS polymer during hot pressing. SBS crumb was pressed at 140^{o}C to form a smooth clear cross-linked disc.

In order to produce membranes for ion-selective electrodes an intimate mixture of membrane components is required. The SBS/THF/QAS solution used in solvent casting method was freeze dried to form a polymer film.

TABLE 2.8

Membranes Prepared by Hot Pressing

Code	SBS(g)	ABIN(g)	Type	Amount(g)	%W/W[a]	Comment
HPA	2.5	-	DADMAC	0.0665	2.66	Prepared by coating SBS Crumb with a solution of Smooth membranes were prepared at press tempera of 125°C-135°C. The membr were not cross-linked a some flow lines are visib
HPB	2.5	-	TAEAB	0.0455	1.82	Clear, slightly yellow membrane prepared at pre temperature 140°C cross- linked.
HPC	2.5	-	DADMAC	0.0572	2.30	Smooth, slightly cloudy membrane, not cross-link
HP(ABIN)	2.5	0.0396	TAEAB	0.0464	1.90	Press temperatures of 14 produce cross-linked cle slightly yellow membrane which contain bubbles.
HP(SBS)	2.5	-	-	-	-	Very tough, flexible cro linked membranes prepare at 140°C.

a % W/W QAS/SBS.

DADMAC Diallyldimethylammonium chloride
TAEAB Triallylethylammonium bromide.

Freeze drying has a similar effect on the polymer solution as solvent evaporation, but is far more rapid, resulting in a homogeneous mixture of all components, in the form of a film or fibrous granules. A sample was also prepared by coating SBS crumb with a solution of QAS, and freeze drying the crumb before hot pressing.

Several samples were prepared, processed and examined to evaluate hot pressing as an alternative method of membrane preparation. Details of these membranes are listed in Table 2.8.

d) Method of Membrane Preparation by Hot Pressing

An 'in house design' hydraulic press was used in the preparation of these membranes. The polymer crumb was pressed between stainless steel dies in a sealed compartment. A heating collar was placed over the sample compartment of the press and a thermocouple placed on the lower die to obtain the press temperature. The temperature of the press was allowed to stabilise, then the sample was placed between the dies, the sample compartment was sealed, and the pressure applied (approximately $2.5 \times 10^{4} Nm^{-2}$). The samples were maintained at the pressures and temperatures specified, Table 2.8., for 15-30 minutes. A cooling collar with circulating water was used to lower the press temperature before the pressure was released. The membranes prepared are listed in Table 2.8.

2.3.2.3 The Use of tert-Butylhydroperoxide (tBHP) Initiator.

The use of ABIN and thermal or photochemical initiation produced cross-linked samples of SBS. The ABIN initiator produces radicals which act upon the butadiene double bonds leading to cross-linking. The initiator produces cross-linked membranes in the presence of the QAS and methanol, however it may not initiate reactions with the QAS, only other polymer molecules. It was thought that since the initiator tBHP was used in the polymerisation of unsaturated QAS[84], it should therefore initiate reactions involving the allyl unsaturation. The initiator tBHP was assessed as an initiator for copolymerisation reactions.

Preparation of Membranes using tBHP Initiator

Membrane solutions were prepared by dissolving SBS in THF overnight. The QAS was dissolved in a small amount of methanol ($<2cm^3$) and added to the solution with tBHP while the solution was stirred. The membrane solution was poured into a weighted, glass ring on a sheet of cellophane supported by a glass plate. The casting assembly was then placed in an oven at 60^oC. The membranes were solid within 5-6 hours and the remaining solvent was removed in a vacuum oven at 55^oC. The membranes prepared by this method are listed in Table 2.9. The membrane code H(Table 2.9) showed very promising characteristics and several variations of the original formulation were prepared, Table 2.10.

Table 2.9

Preparation of Membranes with tBHP Initiator

Code	SBS(g)	tBHP(g)	Type	Amount(g)	% W/W[c]	Appearance
A[a]	2.5	0.1150	TAAB	0.0991	3.96	Slightly cloudy
B[b]	2.5	0.1150	TAAB	0.1032	4.13	Clear
C[a]	2.5	0.1150	DADMAC	0.1059	4.24	Clear with cloudy streaks
D[b]	2.5	0.1150	TAMAB	0.1011	4.04	V.clear
E[b]	2.5	0.0100	TAAB	0.1052	4.21	Slightly cloudy
F[a]	2.5	0.0290	TAAB	0.1000	4.00	Absolutely clear
G[b]	2.5	0.0140	DADEAC	0.2947	11.79	Cloudy and greasy
H[a]	2.5	0.0192	TAEAB	0.2540	10.16	Slightly yellow

a 95 mm Ring

b 70 mm Ring

c % W/W QAS/SBS

TAAB Tetrallylammonium bromide

DADMAC Diallyldmethylammonium chloride

TAMAB Triallylmethylammonium bromide

DADEAC Diallyldiethylammonium chloride

TAEAB Triallylethylammonium bromide

TABAB Triallylbutylammonium bromide

Table 2.10

Preparation of Membranes with tBHP Initiator Based on the Membrane H

Code	SBS(g)	tBHP (g)	Type	Amount(g)	% W/W[a]
MAY 6	2.52	0.0255	TAEAB	0.2590	10.28
MAY 7	2.50	0.0413	TAEAB	0.2588	10.35
MAY 8	2.52	0.0634	TAEAB	0.3750	14.81
MAY 9	2.50	0.1102	TAEAB	0.3749	15.00
MAY 10	2.50	0.1085	TAEAB	0.2552	10.21
JUNE 1	2.50	0.0606	TAAB	0.2657	10.63
JUNE 2	2.50	0.0557	TAAB	0.1951	7.80
JUNE 3	2.50	0.0488	TABAB	0.2859	11.44
JUNE 4	2.50	0.0497	ATEAB	0.2303	9.21
JUNE 5	2.50	0.0487	DADPAB	0.2684	10.74
JUNE 6	2.50	0.0516	TAMAB	0.2413	9.65
JUNE 7	2.50	0.0466	DADEAB	0.2431	9.72
JUNE 8	2.50	0.0468	DADEAC	0.2969	11.88
JUNE 9	2.50	0.0564	TAPAB	0.2691	10.76

Cast in 70mm Ring

a % W/W QAS/SBS

TAAB Tetraallylammonium bromide
TABAB Triallylbutylammonium bromide
TAPAB Triallylpropylammonium bromide
TAEAB Triallylethylammonium bromide
TAMAB Triallylmethylammonium bromide
DADPAB Diallyldipropylammonium bromide
DADEAB Diallyldiethylammonium bromide
DADEAC Diallyldiethylammonium chloride
ATEAB Allyltriethylammonium bromide

CHAPTER 3

TECHNIQUES FOR MEMBRANE EVALUATION

The polymer membranes described in Chapter 2 were characterised and evaluated in several ways. The electroanalytical properties of the polymer membranes are perhaps the most important; they give an indication of their usefulness as nitrate responsive membranes. The structure of the polymer membranes was also assessed by the extent of cross-linking and the amount of covalently bound nitrogen. The cross-linked density was evaluated by equilibrium swelling measurements using the Flory-Rehner theory. The amount of covalently bound nitrogen was determined by Kjeldahl analysis.

3.1 Electroanalytical Properties

3.1.1 Membrane Potentials and the Nernst Equation

The principle of ion-selective electrode response was described briefly in Section 1.3.1. A full description will not be attempted here, but a summary of the most relevant aspects will be given. The reader is referred to the following texts,[96,97,98,99] where the theory has been extensively covered, for a fuller treatment.

When an ion-selective electrode is immersed in a solution a potential is generated across the membrane as a result of the activity of the ion of interest in the external solution. The magnitude of this potential is related to the difference in the activity of the ion in the internal and external solutions. The activity of the ion in the internal filling solution is constant, so the magnitude of the potential is related to the activity of the ion in the external solution. The membrane potential cannot be measured directly but can be determined from the emf of a complete electrochemical cell. The cell can be described as:

Electrode 1/Solution A/Membrane/Solution B/Electrode 2

Electrode Potential	Membrane Potential	Electrode Potential

Electrode 1 is an external reference electrode, a calomel electrode is often used. The early electro-analytical measurements for this project were performed with a simple calomel electrode, later work involved the use of a double junction electrode with a sulphate bridge solution. Electrode 2 is the internal reference electrode, a silver, silver chloride electrode was used for this work. Hence the cell can be defined:

$$\underbrace{Hg/Hg_2Cl_2/\text{Sat'd KCl/Sat'd } K_2SO_4}_{E_{ref}}\,/\!/\;\;E_j$$

$$\text{Test Soln/ISE Membrane/Internal Filling Solution / AgCl/Ag}$$

$$E_m \qquad E'_{ref}$$

The overall potential of the cell E_{cell} is made up of a number of contributions from the components of the cell.

$$E_{cell} = E_{ref} + E_j + E_m - E'_{ref}$$

E_{ref} and E'_{ref} are the potentials of the two reference electrodes; E_j is the sum of the liquid junction potentials; E_m is the membrane potential. The liquid junction potential E_j, and the potential of the reference electrodes are assumed to remain constant for a particular cell, when the temperature is controlled and an ionic strength adjustment buffer is used to produce test solutions of uniform ionic strength. The changes in E_{cell}, which occur under these conditions, are due to changes in the membrane potential E_m. The membrane potential varies with the activity of the determinand in the test solution.

The Nernst equation relates the overall cell potential of a membrane electrode to the activity of the determinand ion (a_i) and may be written:

$$E = E^{\ominus} + \frac{2.303\ RT}{z_i F} \log_{10} a_i \qquad (3.1)$$

where z_i = the sign and charge on the ion i

$E^{\ominus}$ = a constant for the system which incorporates E_{ref}, E'_{ref} and E_j.

R = the gas constant

T = the absolute temperature

F = the Faraday constant

a_i = the activity of the determinand ion.

For a nitrate selective electrode the Nernst relationship $E_{vs} \log a_i$ is expected to be linear with a slope of -59.2mV per decade change of a_{NO_3} at 25°C. This is the ideal Nernst slope for a univalent anion.

3.1.2 Activity and Activity Coefficients

Ion-selective electrodes measure the activity of a given ion in solution. It is the activity which is responsible for the magnitude of the potential generated at the electrode membrane. The activity of anion (a_i) in solution may be related to its concentration (c_i) by the equation,

$$a_i = c_i \gamma \qquad (3.2)$$

where γ is the activity coefficient. The Debye-Hückel

theory made possible the calculation of the mean activity coefficients of dilute electrolyte solutions without the need for experimental measurement. The activity of any ion in solution can only be considered in relation to all the ions present, not in isolation. The Debye-Hückel theory was derived from statistical and electrostatic considerations of ions in solution, by considering the charges on the ions, their concentrations and the properties of the solvent.

The total ionic strength is the sum of all the ions in the solution and is expressed by:-

$$I = \tfrac{1}{2} \sum c_i z_i^2 \qquad (3.3)$$

where c_i is the concentration in mol.l^{-1} and z_i is the ionic charge. The Debye-Hückel equation:-

$$\log \gamma = -Az^2 I^{\frac{1}{2}} \qquad (3.4)$$

is used for determining ionic activity coefficients, where: γ is the activity coefficient; z is the charge; I is the ionic strength of the solution; A is a constant which is dependent on the temperature and the solvent (A = 0.511 for water at 25°C).

The Debye-Hückel equation (3.4) applies at zero ionic strength, real solutions depart from the approximation at high concentrations. The theory predicts

that the activity of an ion depends only on its charge and ionic environment, other ions are not considered beyond the specification of their charge. The activity coefficient is expected to decrease uniformly as the ionic strength of the solution increases. However with increasing ionic strength the presence of other ions in the solution bring into play electrostatic forces which are not accounted for by the Debye-Hückel theory and real solutions depart from the predictions of the theory. Several empirical extensions of equation 3.4 have been used by other workers in an attempt to fit the observed deviation from theoretical predictions. The extension of the Debye-Hückel equation used throughout this work to calculate ion activities was;

$$\log \gamma_{NO_3^-} = -z^2 \left[\frac{AI^{\frac{1}{2}}}{1+I^{\frac{1}{2}}} - 0.2I \right] \qquad (3.5)$$

which was found to give adequate fit to the observed behaviour. The theoretical considerations of the equation 3.5 will not be discussed. The topic is covered extensively in other publications[100,101].

The convention

$$pNO_3 = -\log a_{NO_3^-}$$

has also been adopted without discussion.

3.1.3 Selectivity and Selectivity Coefficients

The ideal ion-selective electrode which is specific for a single ion has never been realised. Ion-selective electrodes may respond to several ions, but a useful electrode will respond preferentially to a particular ion. Under certain circumstances the response to the chosen ion will be affected by the presence of other ions, the electrode will suffer interference. The extent of the interference requires definition and measurement.

The term 'potential selectivity coefficient' k_{AB}^{Pot} defines the ability of an ion-selective electrode to distinguish between different ions in the same solution[102]. The selectivity coefficient is best evaluated by means of the emf response in mixed solutions of the primary ion A and the interferent B. An alternative method involves measurement of the emf for separate solutions. The value k_{AB}^{Pot} is defined by the modified Nernst equation:

$$E = E^{\ominus} + \frac{2.303\ RT}{z_A F}\log\ (a_A + k_{AB}^{Pot}\ (a_B)^{z_A/z_B} + k_{A,C}^{Pot}\ (a_C)^{z_A/z_C} \ldots\ldots) \qquad (3.6)$$

where:

E = the experimentally observed potential of the cell.

$E^{\ominus}$ = a constant.

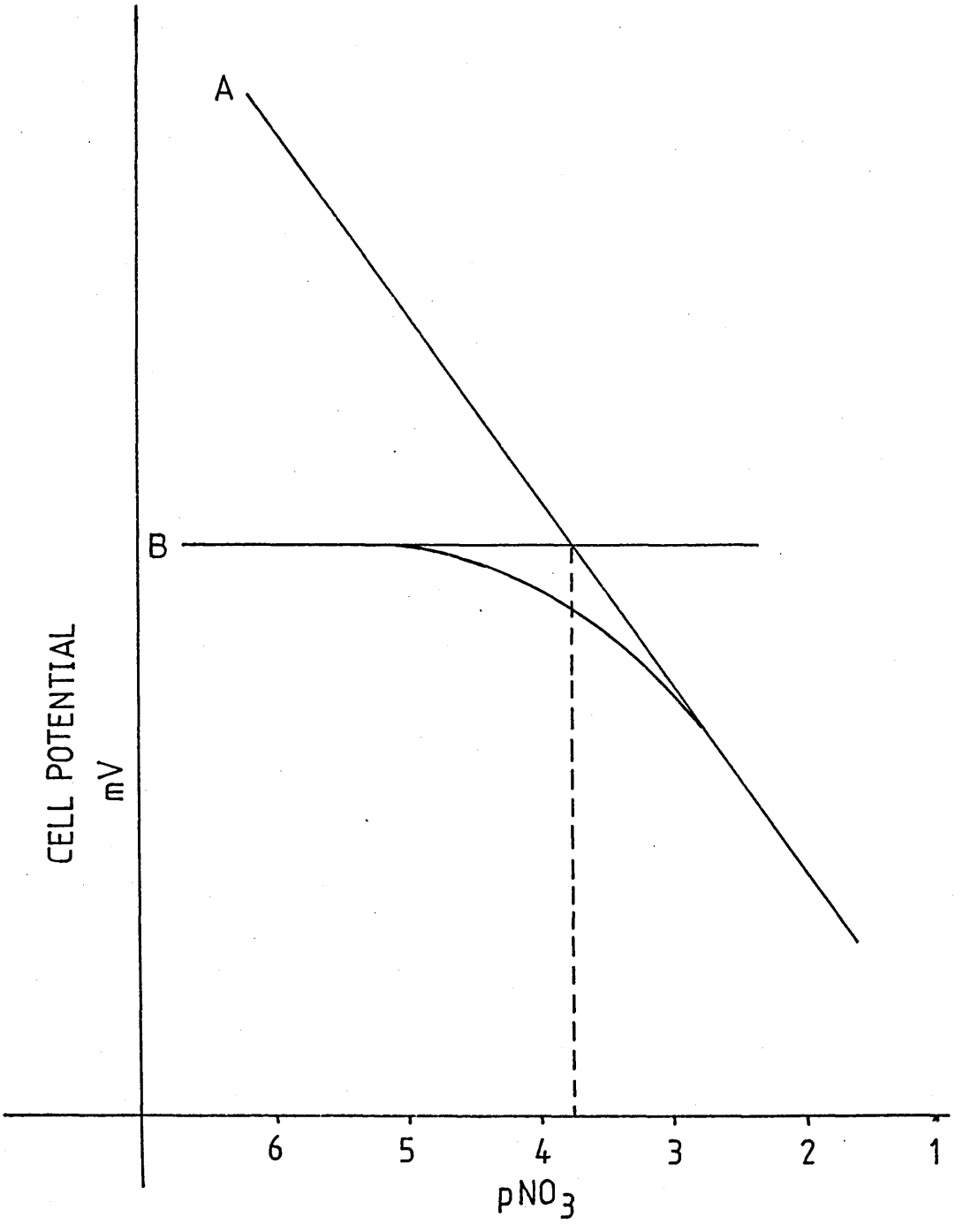


Fig.3.1 Calculation of selectivity coefficient k_{AB}^{Pot}.

R = the gas constant

T = the absolute temperature

F = the Faraday constant

a_A = the activity of the ion A

a_B, a_C = the activities of the interfering ions B and C respectively.

k_{AB} = the potentiometric selectivity coefficient

z_A, z_B, z_C = the sign and charge of the ions A, B and C respectively

The smaller the value k_{AB}^{Pot} the greater the electrodes preference for the principal ion. However the value k_{AB}^{Pot} is only meaningful if accompanied by the experimental conditions and the method by which it was obtained.

3.1.3.1 Mixed Solution Method[99]

The response of the ISE is monitored using standard solutions of the primary ion A with a fixed level of the interferent ion B. A typical nitrate ISE response is shown in Figure 3.1 with a typical chloride interference curve. The response to the primary ion deteriorates with decreasing activity of that ion in the solutions. The calibration curve eventually shows a plateau. The plateau is the response of the electrode to the constant background of interferent,

and is the limiting potential of the response. The selectivity coefficient is determined as a limit of detection. The intercept of the two vertical sections of the calibration plot (Figure 3.1) defines a particular activity of the primary ion. The selectivity constant may then be calculated as $a_A = k_{AB}$. Where a_B is the activity of the interferent ion. The point of intersection is the point at which the electrode responds equally to both ions. From equation 3.6

$$k_{AB}^{Pot} = \frac{a_A^{z_A}}{a_B^{z_B}} \qquad (3.7)$$

In some cases the ion-selective electrode is subject to high interference, resulting in drift and irreproducibility in the plateau region, the calibration will not consist of two linear parts, but a linear Nernstian region and a curved region of interference. This effect is also produced when the electrode responds to both the ions in the solution. Both ions are said to be contributing to the observed potential when;

$$a_A = k_{AB}^{Pot} \, a_B^{\,z_A/z_B} \qquad (3.8)$$

If $z_A = z_B = 1$ then equation 3.6 becomes;

$$E = E^{\circ} + \frac{2.303RT}{F} \log_{10}(a_A + k_{AB}^{Pot} \, a_B) \qquad (3.9)$$

Substituting equation 3.8 into equation 3.9 gives;

$$E = E^{\ominus} + \frac{2.303RT}{F} \log_{10}(2a_A) \qquad (3.10)$$

The difference between the potential of the electrode in a solution of ion A, and a solution of ion A with interferent ion B can be expressed as the difference between the Nernst equation 3.1 for ion A and equation 3.10

$$E = \frac{2.303RT}{F} (\log_{10} 2a_A - \log_{10} a_A)$$

$$= \frac{2.303RT}{F} \log_{10} 2$$

$$= 17.8\text{mV at } 25^{\circ}\text{C}$$

The required activity of the primary ion may be located, in situations of high interference for univalent ions, by taking the point on the experimental potential curve where it differs by 17.8mV from the extrapolated Nernstian line.

The reverse situation is also used. The interfering ion is varied against a constant level of primary ion. This method is commonly used for examining H^+ interference in fixed primary ion solutions with varying pH levels.

Mixed solution methods are advantageous because they present an immediate picture of real situations. The calibration plots can be used for a visual assessment of the interference.

3.1.3.2 Separate Solution Methods

Potential measurements are made using the ion-selective electrode in two separate solutions, one containing the primary ion A, the other the interferent ion B at the same activity

$$a_A = a_B$$

If the measured values are E_1 and E_2 respectively the k_{AB}^{Pot} may be calculated from the difference in the potential response

$$E_1 = E^{\ominus} = \frac{2.303RT}{zF} \log a_A \qquad (3.11)$$

$$E_2 = E^{\ominus} + \frac{2.303RT}{zF} \log k_{AB}a_B \qquad (3.12)$$

E_1 = the potential of the primary ion solution

E_2 = the potential of the interferent solution

E = the potential of the mixture

$$E = E^{\ominus} + \frac{2.303RT}{zF} \left[\log a_A + k_{AB}a_B\right] \qquad (3.13)$$

$$\therefore \quad E_2 - E_1 = +\frac{2.303RT}{zF} \left[\log k_{AB} + \log a_B - \log a_A\right] \qquad (3.14)$$

If the activities of the primary ion and interferent ion are equal in the two solutions the equation becomes:-

$$\frac{E_2 - E_1}{2.303RT/zF} = \log k_{AB} \qquad (3.15)$$

The selectivity coefficient is readily obtained from the difference in potential in the two solutions. The

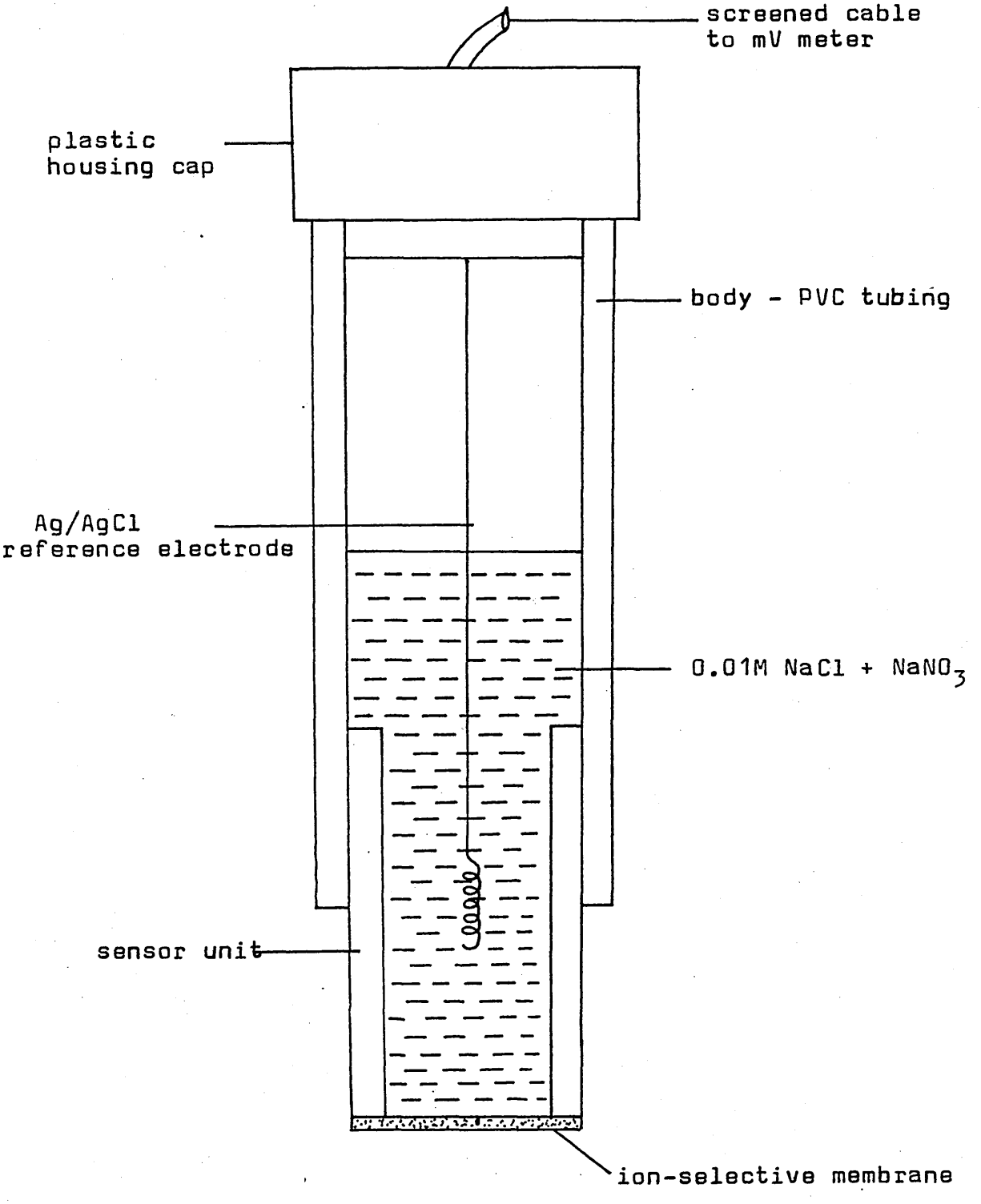


Fig.3.2 The 'In house' Design Electrode Body

calculation needs some modification for interferent ions with different charges.

3.2 Experimental

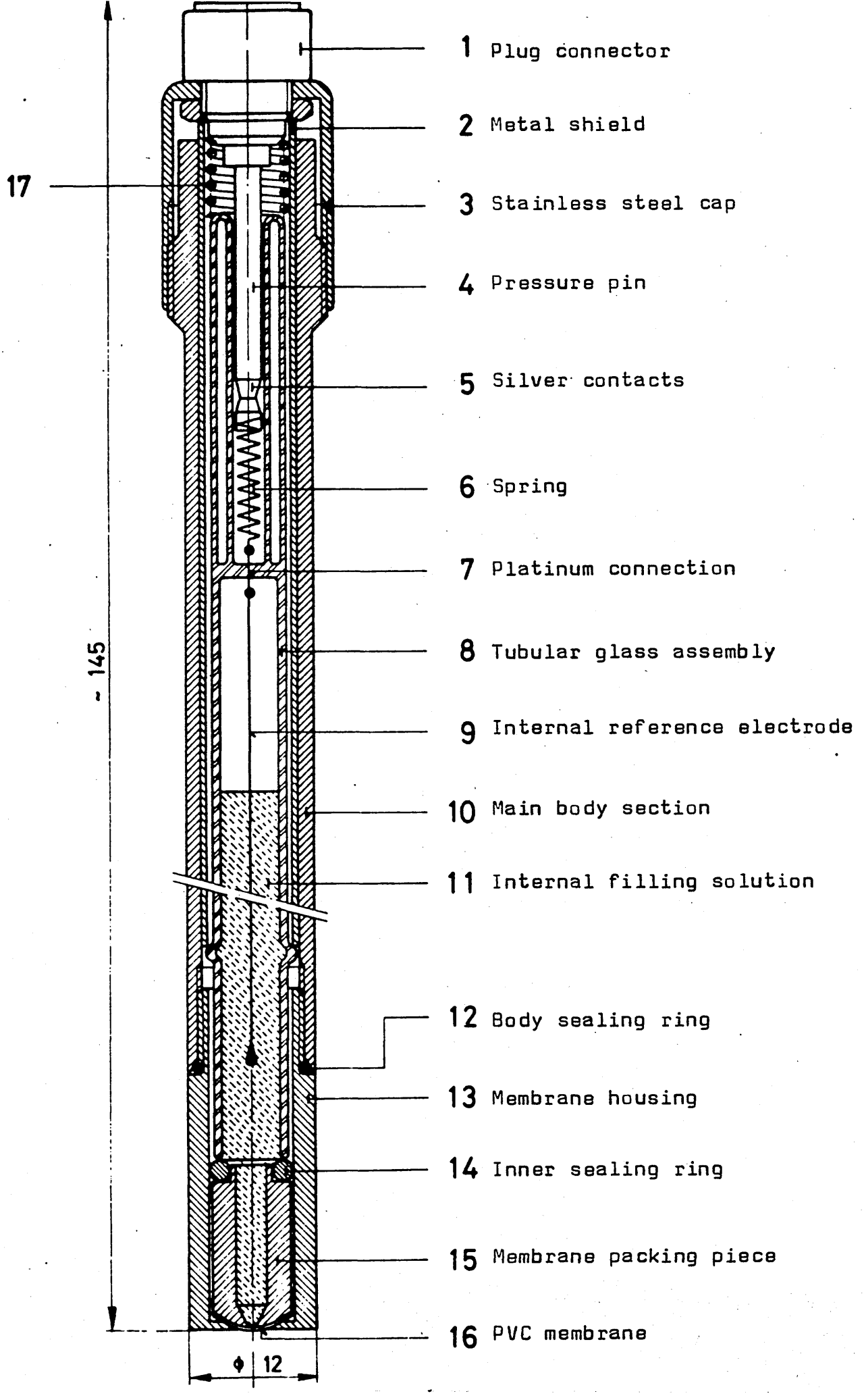
3.2.1 Equipment

3.2.1.1 Electrode Construction

The method used for screening the early polymer membranes involved the use of an 'in house' design electrode body with interchangeable sensor units. The majority of membranes however were screened using a commercial electrode body Philips IS561 (Philips Analytical, York Street, Cambridge). The construction of the electrode allowed individual polymer membranes to be interchanged for evaluation. The Philips electrode body was modified in several ways to enable rigid polymers to be examined. The procedures involved with the different electrode constructions are described below.

3.2.1.2 The 'in house' Design Electrode

The electrode body is illustrated in Figure 3.2. The main body of the electrode consisted of a clear plasticised PVC tube, push-fitted to a plastic cap. The plastic cap housed the electrical connection between the Ag/AgCl reference element and the copper wire which lead to the millivolt meter. The internal filling solution was a 50% v/v mixture of 10^{-1} mol dm^{-3} $NaNO_3$ and 10^{-1} mol dm^{-3} NaCl. Sensor units were prepared, rinsed with


1 Plug connector
2 Metal shield
17
3 Stainless steel cap
4 Pressure pin
5 Silver contacts
6 Spring
7 Platinum connection
8 Tubular glass assembly
~ 145
9 Internal reference electrode
10 Main body section
11 Internal filling solution
12 Body sealing ring
13 Membrane housing
14 Inner sealing ring
15 Membrane packing piece
16 PVC membrane
ϕ 12

de-ionised water and push-fitted to the electrode body.

3.2.1.3 The Sensor Unit

A disc was cut from each polymer membrane using a 9mm cork-borer, and attached to a piece of clear plasticised PVC tubing (3cm in length, 9mm in diameter) using a waterproof adhesive. The unit was allowed to dry for several hours. The membrane was then conditioned by immersing the sensor unit in a 10^{-1} mol dm^{-3} solution of $NaNO_3$.

3.2.1.4 The Commercial Electrode

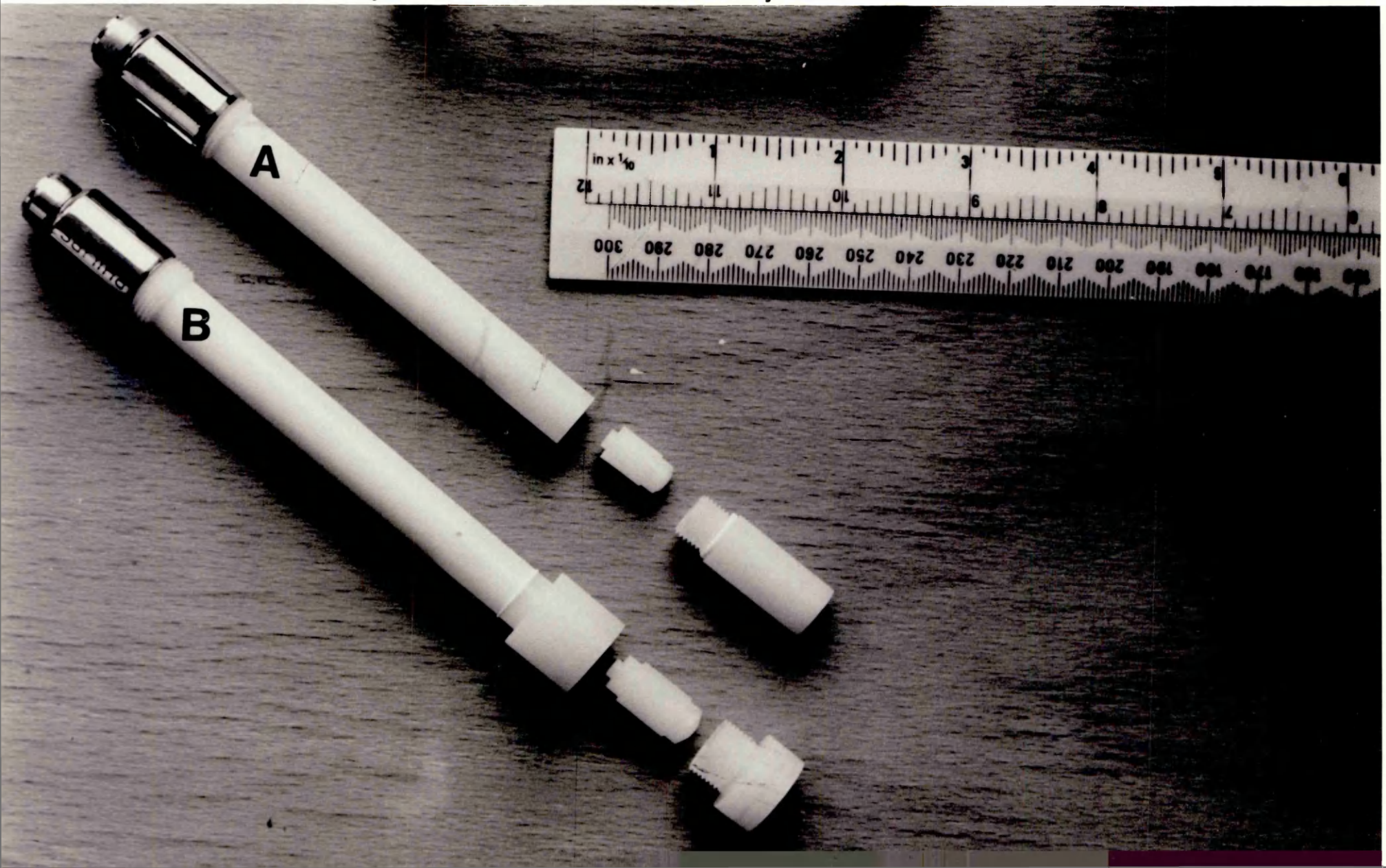
The Philips electrode body enabled membranes to be interchanged for evaluation. The membranes were secured without the aid of an adhesive. The commercial electrode body illustrated in Figure 3.3 was modified to expose a larger area of membrane to the testing solutions. This was accomplished by using an 'in house' designed extension to the original electrode. The original electrode and the modified electrode are illustrated in Plate 3.1. The internal, glass electrode body was replaced by an identical unit fashioned from teflon. The glass, internal reference unit was extremely fragile and unsuitable for use with membranes of a tough and relatively rigid nature.

The membranes were conditioned prior to use and stored individually in conditioning solution.

PLATE 3.1

THE MODIFIED PHILIPS ELECTRODE BODY

A. The commercial electrode body. B. The modified electrode body.



3.2.1.5 Reference Electrodes

The reference electrode in the early experiments was a simple calomel electrode. A double junction calomel electrode CRR/DJ/2 (Russel pH Ltd, Auchtermuchty, Fife), with a sulphate bridge solution was used in later work. The double junction electrode prevented contamination of the test solutions, and ultimately the polymer membranes, with chloride which can leach from the calomel electrode.

3.2.1.6 Meters

Potential measurements were made with a Philips PW 9409 (Philips, Pye Unicam, York Street, Cambridge, UK), and a Pye Model 290pH Meter (Pye Unicam, Cambridge). The meters had an input impedance of $10^{12}\Omega$ and $5\times10^{12}\Omega$ respectively. The meters were used to a precision of $\pm$ 1mV.

3.2.1.7 Ancillary Equipment

General potential measurements were performed at $25^{o}C \pm 1^{o}C$ in stirred solutions. Measurements were made with $50cm^{3}$ of test solution in a $150cm^{3}$ Pyrex beaker with an insulating jacket. Selectivity coefficients were determined at $25^{o}C \pm 0.25^{o}C$, with stirring, by immersing the Pyrex beaker in a thermostatted water bath. The test solutions were stored in a water bath at $25^{o}C$ for all calibrations. Stirring of the test solution was accomplished using a magnetic stirrer at

constant speed and a teflon coated stirrer bar.

3.2.2 Experimental Procedures

3.2.2.1 Conditioning

The membranes were conditioned before use in 10^{-1} mol dm^{-3} $NaNO_3$ solution for 24 hours, and stored between tests in this solution. The membranes were rinsed and dried prior to and after each calibration.

3.2.2.2 Standard Solutions

Standard solutions were prepared daily using analytical reagent grade material and stored for the minimum period before use. Standard solutions were prepared from potassium nitrate (AnalaR Grade, BDH Chemicals, Poole, Dorset) dissolved in de-ionised, double distilled water. A range of standards 10^{-1} - 10^{-5} mol dm^{-3} were prepared by serial dilution of freshly prepared 10^{-1} mol dm^{-3} solution or from 1 mol dm^{-3} stock solution.

A potassium dihydrogen orthophosphate buffer (AnalaR Reagent, BDH) was used for some electrode calibrations. Standard solutions were prepared with 10^{-2} mol dm^{-3} background of this buffer. The standard solutions and the equipment were calibrated by using a commercial nitrate electrode (Philips IS561 NO_3^- Plastic Membrane Electrode).

3.2.2.3 Interference Work

The interference of other ions was assessed using a mixed solution method. The electrodes were calibrated using either prepared solutions or by spiking nitrate standards with the interferent ion. The first method involved the preparation of nitrate standards containing 10^{-2} mol dm^{-3} of the interferent ion, the electrodes were calibrated in accordance with the procedure for nitrate standards. The second method involved the calibration of the electrode with 50cm^3 of a nitrate stock solution, the 1.0 mol dm^{-3} interferent solution was introduced using a 500μl automatic pipette (Oxford Sampler Micropipetting System).

3.2.2.4 Calibration Technique

Calibrations were established by serial measurements of standard solutions. A fresh solution was used for each measurement. The calibration was usually performed using the most dilute solution first; electrodes were blotted with tissue between each test. If the solutions were used in the opposite order, commencing with the most concentrated, then the electrodes were rinsed with de-ionised distilled water and blotted with tissue.

The response was recorded after 2 min. or in dilute solution after 5 min. The response time of the electrode depends on a number of parameters including temperature,

conditioning, pretreatment, stirring rate, and the activity of the test solution. The electrodes were judged to have reached 95% of their response value after 2 min. for solutions 10^{-1} - 10^{-4} mol dm^{-3}. The response time for 10^{-5} mol dm^{-3} solution was generally observed to be longer and 5 min. were usually allowed for 95% of final response.

Response time behaviour was assessed by recording the potential of the cell at intervals of 15s for 2 min.

Calibration graphs were constructed by plotting emf response against pNO_3.

3.3 Cross-linked Density

3.3.1 Cross-linking of Polymer Chains

The chemical reaction of individual polymer chains, to form bonds, results in the formation of an infinite, three dimensional network. Such polymer networks are insoluble in all solvents except for those which disrupt the chemical structure of the polymer. They do not undergo appreciable plastic or viscous flow. Cross-linking is usually assumed to be exclusively intermolecular among finite species. Every cross-linkage which occurs decreases the number of molecules by one. Cross-linking will eventually lead to the formation of a gel (solid polymer, no longer in solution). The

higher the molecular weight of the polymer units the less cross-links are required before gelation.

3.3.2 Calculation of Cross-Linked Density

The calculation of cross-linked density is based on the kinetic theory of rubber elasticity. The theoretical considerations and resulting solutions were derived independently by a number of workers including Wall[103], and Flory and Rehner[104]. They based their evaluations upon the entropy of the network structure by considering the structure at various stages. First the entropy of an individual polymer molecule was considered; the polymer molecule was replaced by a chain; the chain was then restricted to a specific conformation; and eventually an ideal network was envisaged and the entropy of the network at equilibrium was determined. In order to calculate the cross-linked density the network was deformed. The entropy of the deformed network was evaluated and compared to the change in entropy which occurred upon deformation. The change in entropy was then related to the numbers of cross-links. In general the greater the number of cross-links, the more rigid and less elastic the polymer and the greater the force required to deform the network.

Cross-link density can be derived from equilibrium swelling measurements. A three dimensional network structure is incapable of dispersing completely, but is able to absorb a large quantity of the solvent, with which it is in contact. Swelling occurs for the same reason that a solvent mixes spontaneously with an analogous linear polymer, to form a solution. The swollen gel may be considered as an elastic solution rather than a viscous one. The polymer swells assuming an increased volume, throughout which the solvent is able to spread, therefore an opportunity is presented for an increase in entropy. The mixing tendency, or entropy of dilution, is also influenced either positively or negatively by the heat of dilution. As the network is swollen by absorption of solvent, the polymer chains between crosslinks become elongated. Forces similar to the elastic retractive force in rubber develop in opposition to the swelling process. As swelling proceeds these forces increase and the diluting force decreases until a state of equilibrium is reached when the two are balanced.

Swelling equilibrium is analogous to osmotic equilibrium. The elastic reaction of the network structure may be interpreted as a pressure acting on the solution or swollen gel. In the equilibrium state this

pressure is sufficient to increase the chemical potential of the solvent in the solution to equal that of the excess solvent surrounding the swollen gel. Thus the network structure performs the roles of solute, osmotic membrane and pressure generating device.

3.3.3 The Flory-Rehner Equation

The theoretical and mathematical considerations of this work were covered in depth by Flory[105].

The mathematical considerations involved with the derivation of this equation are too complex for discussion in this work. The final equation and the parameters involved are presented and explained in the context of the experimental data required for the calculation. By consideration of the polymer-solvent solution thermodynamics introduced above, the following relationship was proposed for a cross-linked elastomer at equilibrium:[106]

$$B = \frac{-(v_2^{1/3} - v_2/2)}{\ln(1-v_2)+v_2+\mu v_2^2} \qquad (3.16)$$

B = the ratio of the volume of a chain to the volume of a solvent molecule.

v_2 = the reciprocal of the equilibrium swelling volume ratio.

μ = the polymer solvent interaction parameter

Let: $B = \frac{M_c}{\rho V_1}$

M_c = number average molecular weight of cross-links.

ρ = density of the polymer

V_1 = molar volume of the solvent.

Then $$M_c = -\frac{\rho V_1 (v_2^{1/3} - v_2/2)}{\ln(1-v_2) + v_2 + \mu v_2^2} \qquad (3.17)$$

If $N = \frac{\text{moles of cross-links}}{\text{volume of polymer}}$

Then $$\ln(1-v_2) + v_2 + \mu v_2^2 = -NV_1(v_2^{1/3} - v_2/2) \qquad (3.18)$$

The experimental parameters required for this calculation are v_2, μ and V_1.

The reciprocal of the equilibrium swelling volume ratio, v_2 was determined from the swollen weight of the polymer[107].

$$s = \frac{m-m_o}{m_o} \qquad (3.19)$$

where m_o and m are the weights of the test specimen before and after swelling respectively.

The volume fraction of the elastomer in the swollen gel is then determined from:

$$v_2 = \frac{1}{1 + \left(\frac{\rho_2}{\rho_1}\right) s} \qquad (3.20)$$

where:

ρ_1 = the density of the swelling liquid

ρ_2 = the density of the unswollen polymer.

The polymer may contain entangled chains, or other soluble fractions, which are removed from the polymer during swelling. The loss of material will result in a decrease in weight. The true equilibrium swollen weight is determined when all soluble material has been removed from the polymer leaving only the cross-linked network. This is achieved by repeated swelling and drying of the polymer until no further decrease in weight is observed. For this work the value m_o was usually taken as the final, dried weight of polymer after 24 hours swelling. Hence, some allowance was made for the presence of soluble material within the polymer, without involving extensive experimental work.

Polymer-solvent interaction parameters, μ have been calculated for a number of solvents and polymers and are easily obtained from standard references. The molar volume of an organic solvent, V_1, is a standard parameter.

3.3.4 Experimental

The average cross-linked density was determined for the polymer membranes prepared by the methods described in Section 2.3. The average cross-linked density was calculated using three random samples from the polymer to determine the density of the polymer, and three further samples to determine the swollen weight.

The solvent chosen to perform the swelling tests was heptane (S.L.R. Fisons, Loughborough, England). The polymer samples became turgid when immersed in heptane. However, the cohesion of the samples was sufficient to enable their manipulation in the swollen state.

3.3.4.1 Determination of Swollen Weight[108].

Three random samples were taken from each polymer and weighed. The samples were immersed in excess heptane in a sealed glass tube. The samples were allowed to stand for 24 hours. The swollen samples were removed from the solvent, blotted with soft tissue to remove excess solvent, and weighed in a sealed tube. The procedure was performed rapidly to prevent evaporation of the solvent. The temperature of the solvent was recorded. The samples were dried for 24 hours. A vacuum oven was used to remove the final traces of solvent before the samples were reweighed.

3.3.4.2 Determination of Density

Three random samples were taken from each polymer membrane and weighed. A $50cm^3$ glass density bottle was cleaned, dried and weighed. The density bottle was then accurately filled with water and reweighed. A sample of polymer was placed in the bottle, the bottle was again filled accurately with water and

weighed. The temperature of the water in the density bottle was recorded. The exterior of the density bottle was dried after each addition of water and care was taken to ensure that no air bubbles were trapped around the polymer sample.

3.3.4.3 Calculation of Cross-linked Density

The standard parameters required for the calculation of cross-linked density are the molar volume of heptane, V_1 = 147.5 cm^3 at 25°C, and the polymer-solvent interaction parameter for the SBS triblock polymer in heptane,[109] μ = 0.589 (28.5% styrene, 71.5% butadiene SBS). The polymer solvent interaction parameter does not allow for the presence of quaternary ammonium salts within the polymer network.

The cross-linked density was calculated using a short computer program, Appendix 1.

3.4 Kjeldahl Analysis

The extent of the covalent attachment of nitrogen, to the backbone of the SBS polymer, was assessed using the Kjeldahl reaction,[110,111]. The Kjeldahl reaction is a standard, wet chemical method for the analysis of organic nitrogen. Samples are digested using concentrated sulphuric acid and a mercury catalyst. The digest is performed by heating the mixture in a long-necked flask

until the solution is clear and colourless. The sample is allowed to cool and is then diluted with deionised water. The nitrogen released by the digest is trapped in the solution as ammonium sulphate. When the sample is made strongly alkaline, ammonia is released and distilled from the sample into excess boric acid containing an indicator solution. The solution is then titrated using a standard acid to a pH of about 4.5.

The analytical technique was adjusted to micro-scale [112] because only small quantities of polymer were available. The polymer membranes were analysed in triplicate. The location of each sample in the polymer was noted. A blank digest was performed with each batch of samples. A weak standard acid was used for titrations to allow maximum sensitivity. For every milliequivalent of acid there is a milliequivalent of ammonia and a milligram atom of nitrogen.

3.4.1 Experimental

3.4.1.1 Reagents

Nitrogen free, concentrated sulphuric acid 'Spectrosol L' (BDH, Poole, Dorset) 98% H_2SO_4 was used. Kjeldahl catalyst tablets (BDH) were used in the acid digest. The tablets (2.0g) were 20 parts K_2SO_4 1 part HgO. The ammonia was distilled into a 4% Boric Acid indicator solution (BDH, Poole, Dorset).

Standard acid (10^{-2} mol dm^{-3}) was prepared from an ampoule of HCl(0.1 mol dm^{-3}) (BDH, Poole, Dorset). The acid was then diluted 1 : 14 to produce M/140 acid. The alkaline solution was prepared from AnalaR NaOH (500g) dissolved in deionised water and made up to 1 litre. A 0.1 mg ml^{-1} NH_3.N standard solution was prepared using AnalaR NH_4Cl.

3.4.1.2 Method

The polymer samples were weighed and a sample placed in a long-necked flask with a catalyst tablet. Sulphuric acid ($3cm^3$) was allowed to run down the neck of the flask. The flasks were heated until the sulphuric acid refluxed in the neck of the flask, and this was continued until the sample was clear and colourless. The sample was then cooled and diluted with deionised water ($40cm^3$). The sample was transferred to the distillation apparatus which consisted of a round-bottom flask in a heating mantle, a splash head, condenser and a collecting tube. The collecting tube was placed below the indicator solution ($5cm^3$) in a conical flask.

The ammonia was released from the sample by gently running concentrated alkaline solution ($12cm^3$) down the side of the flask before placing it in the distillation apparatus. Ammonia solution was rapidly distilled from the sample. Approximately $30cm^3$ of

distillate were collected. The final distillate was tested with indicator paper to check for the presence of ammonia. The indicator solution was then titrated against the standard acid until a neutral colour was obtained. The accuracy of the method was assessed by digesting $1cm^3$ aliquots of the standard solution. The mean nitrogen content was found to be 0.095 ± 0.009 mg NH_3.N, by this method.

3.5 Resistance Measurements

Cross-linked SBS showed insulating properties with resistances of $> 10^{12}$ ohms. The formation of a network of quaternary ammonium centres in the polymer, or the uptake of conditioning solution should lower the resistance of the polymer. The leaching of quaternary ammonium salts from the polymer network was expected to increase the resistance. These measurements were used as a guide to the structure and usefulness of the polymers. If a master membrane showed a very high resistance, in the 10^{12} ohms region it was unlikely to show any useful response to nitrate.

The resistance of the polymer was measured using an electrometer (Model 610B, Keithley Instruments, Munich, West Germany). A piece of polymer membrane was placed between two brass plates connected to the meter, and current was passed across the plates. The range of measurement was $10^6 - 10^{12}$ ohms.

CHAPTER 4

EVALUATION OF THE MEMBRANES

4.1 Solvent Cast Membranes

The formulation of the first solvent cast, master membranes C1-F3 are listed in Table 2.5. The physical appearance of these membranes was poor. However, the membranes were firm, flexible, slightly elastic and cross-linked. The master membranes were used to prepare sensor units as described in Section 3.2.1.3. The sensor units were conditioned for 24 hours before their response to nitrate was assessed. The conditioning solution, 10^{-1}mol dm^{-3} $NaNO_3$, was used to exchange the chloride or bromide counter-ions of the QAS, for nitrate ions and so prepare the membranes for nitrate response. During the conditioning period the polymer membranes became white and opaque. The electroanalytical properties of these solvent cast membranes are outlined in Table 4.1. The master membranes D1 and F3 produced several useful sensor units which showed reproducible responses to nitrate solutions. Other master membranes showed more variable properties. The membrane D3 produced two sensor units which showed near-Nernstian response to nitrate with slopes of approximately 53mV per decade, but a third sensor unit showed poor response to nitrate with a slope of only 30mV per decade. Sensor units prepared from master membrane F1 showed poor response to nitrate with low slopes; this master membrane was prepared with only 2.19% W/W QAS/SBS and may have insufficient sensors to provide Nernstian

Electroanalytical Properties of Solvent Cast Membranes

Master Membrane	Sensor Unit	Linear Range (mol dm^{-3})	Slope (mV)	Age [a] (days)	Linear Range (mol dm^{-3})	Slope (mV)	Age [a] (days)	QAS	% W/W QAS/SBS
		Buffered Solutions			Unbuffered Solutions				
C1	CMA1	10^{-1}-10^{-3}	-50	10	-	-	-	DADEAB	3.31
C2	CMB1	10^{-1}-10^{-2}	-50	10	-	-	-	DADEAB	3.35
C3	CMC1	10^{-1}-10^{-3}	-16	10	-	-	-	DADEAB	3.30
D1	DMA1	10^{-1}-10^{-3}	-48	33	10^{-1}-10^{-4}	-47	46	DADEAB	3.93
	DMA2	10^{-1}-10^{-3}	-52	33	-	-	-		
	DMA3	10^{-1}-10^{-3}	-52	7	-	-	-		
D2				NO RESPONSE				None	0%
D3	M1	10^{-1}-10^{-3}	-53	64	10^{-1}-10^{-4}	-53	77	DADEAB	5.13
	DMC1	10^{-1}-10^{-3}	-31	33	-	-	-		
	DMC2	10^{-1}-10^{-3}	-51	33	10^{-1}-10^{-4}	-56	46		
E1	EMA1	10^{-1}-10^{-3}	-49	7	10^{-1}-10^{-4}	-53	23	DADEAB	4.05
	EMA2	10^{-1}-10^{-3}	-20	7	-	-	-		
F1	FMA1	10^{-1}-10^{-3}	-34	33	-	-	-	DADEAB	2.19
	FMA2	10^{-1}-10^{-3}	-27	33	-	-	-		
F2	FMB1	10^{-1}-10^{-3}	-21	33	-	-	-	TAEAB	2.89
	FMB2	10^{-1}-10^{-3}	-53	7	10^{-1}-10^{-4}	-39	20		
F3	FMC1	10^{-1}-10^{-3}	-46	33	10^{-1}-10^{-4}	-47	46	TAAB	3.16
	FMC2	10^{-1}-10^{-2}	-57	7	10^{-1}-10^{-4}	-57	20		

- Not examined a. number of days in conditioning solution

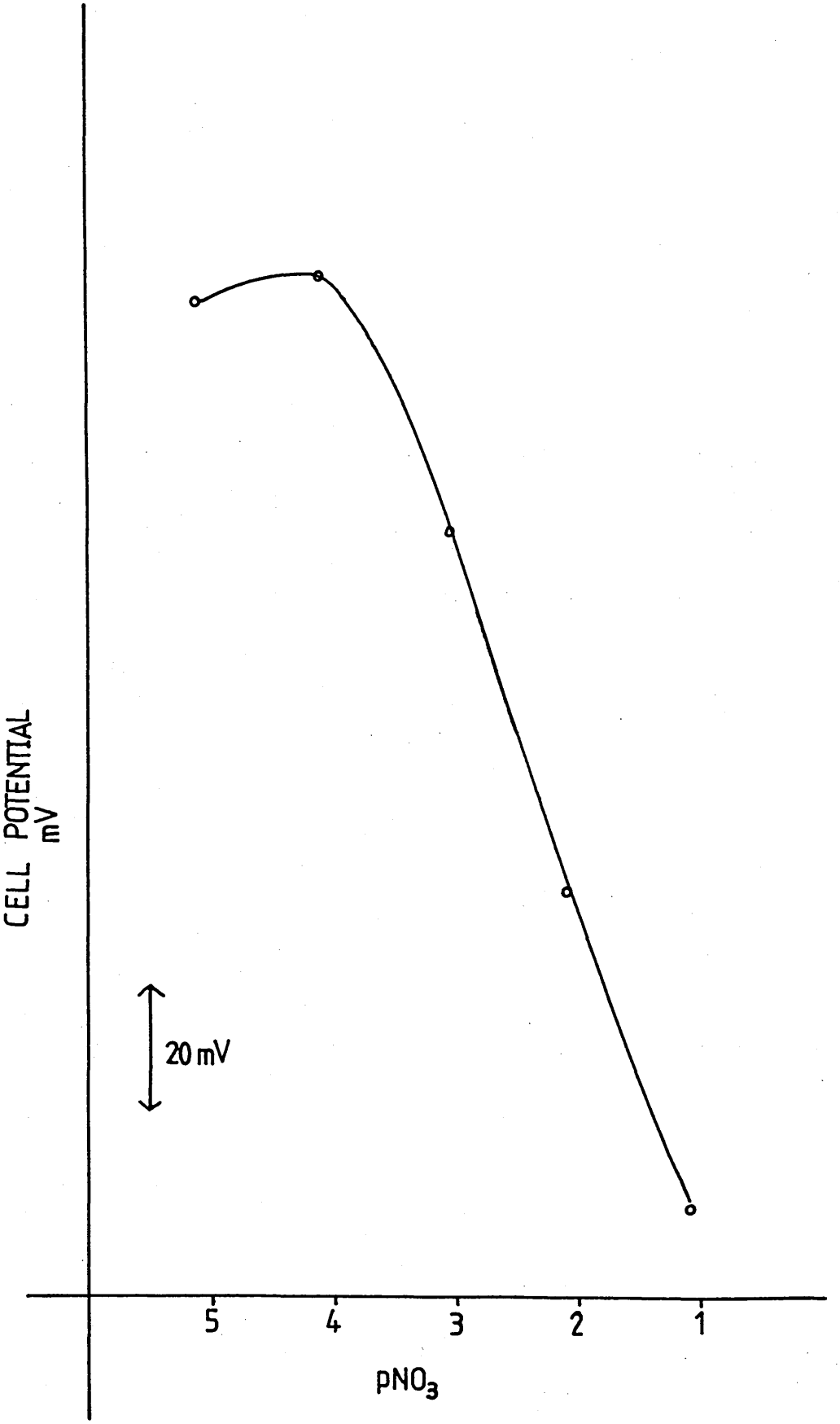


Fig.4.1

The response of electrode M1 to nitrate standards buffered with potassium dihydrogen orthophosphate 10^{-2}mol dm^{-3}, after 89 days conditioning.

response. The master membrane C3 was not exposed to U.V. irradiation and was not cross-linked. Sensor units prepared from the master membrane C3 showed very poor response to nitrate, possibly as a result of the sensor leaching from the polymer. The master membrane D2 showed no response to nitrate, the membrane was prepared by cross-linking SBS polymer without QAS.

A number of sensor units were used several times and stored continuously in conditioning solution over a period of 46 days. The response of these sensor units remained stable during this period. The electrode M1 showed unaltered response over a period of 89 days. Figure 4.1. The true lifetime of the membranes was not assessed; the sensor units were exposed to small volumes of static solutions continuously during storage and were examined for nitrate response intermittently for short periods. A more realistic measure of lifetime would be obtained by exposing the electrodes to a continuous flowing solution.

The response of the sensor units to nitrate was evaluated using nitrate standard solutions containing 10^{-2} mol. dm^{-3} potassium dihydrogen orthophosphate as an ionic strength buffer. The buffer solution did not affect the response of M1, the response of the electrode to buffered and pure nitrate solutions was very similar, see Figure 4.1. and Figure 4.2. The membranes were also exposed to chloride, sulphate and hydroxide ions to assess their selectivity for nitrate. The selectivity of the membranes was examined using

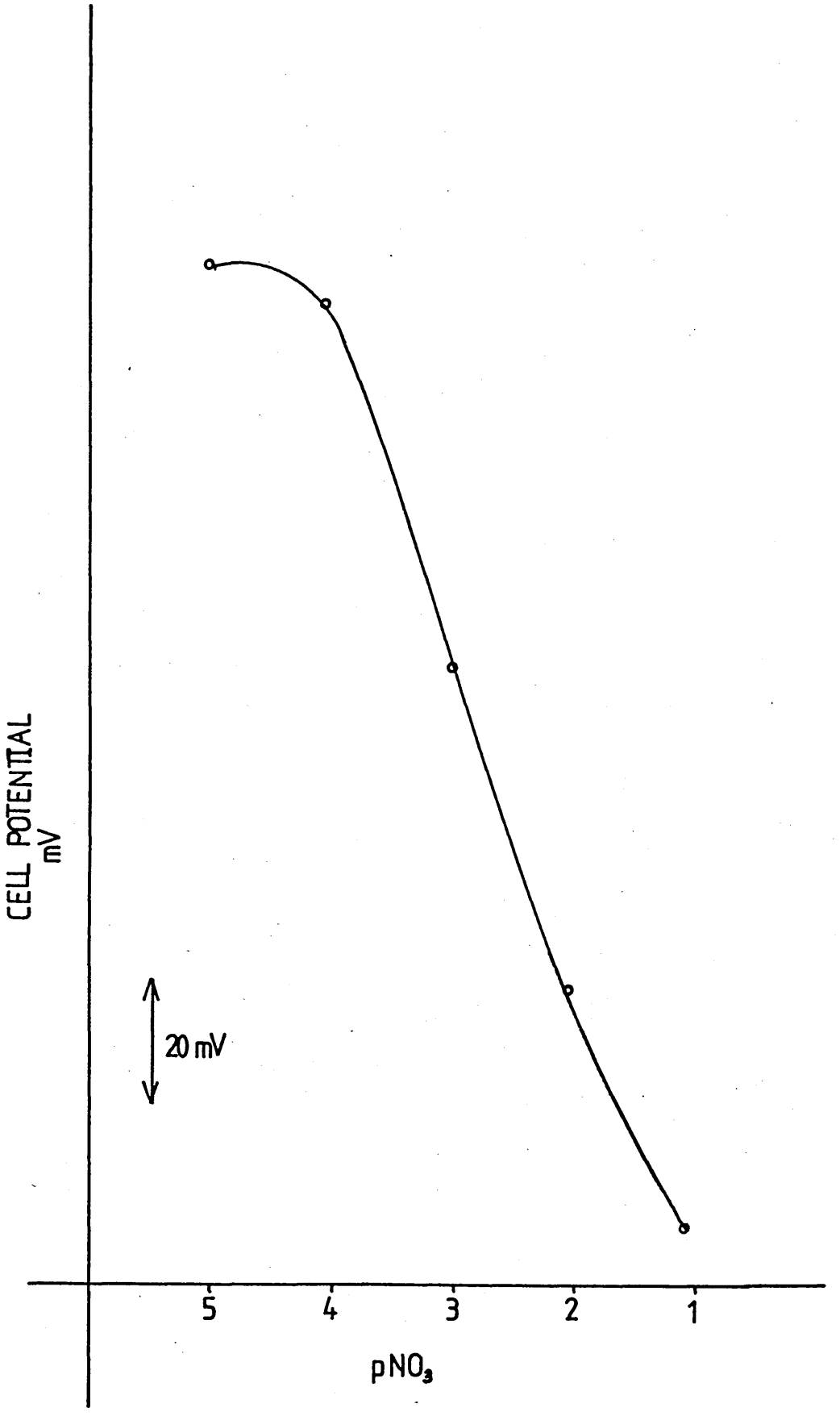


Fig.4.2
The response of electrode M1 to pure nitrate standard solutions.

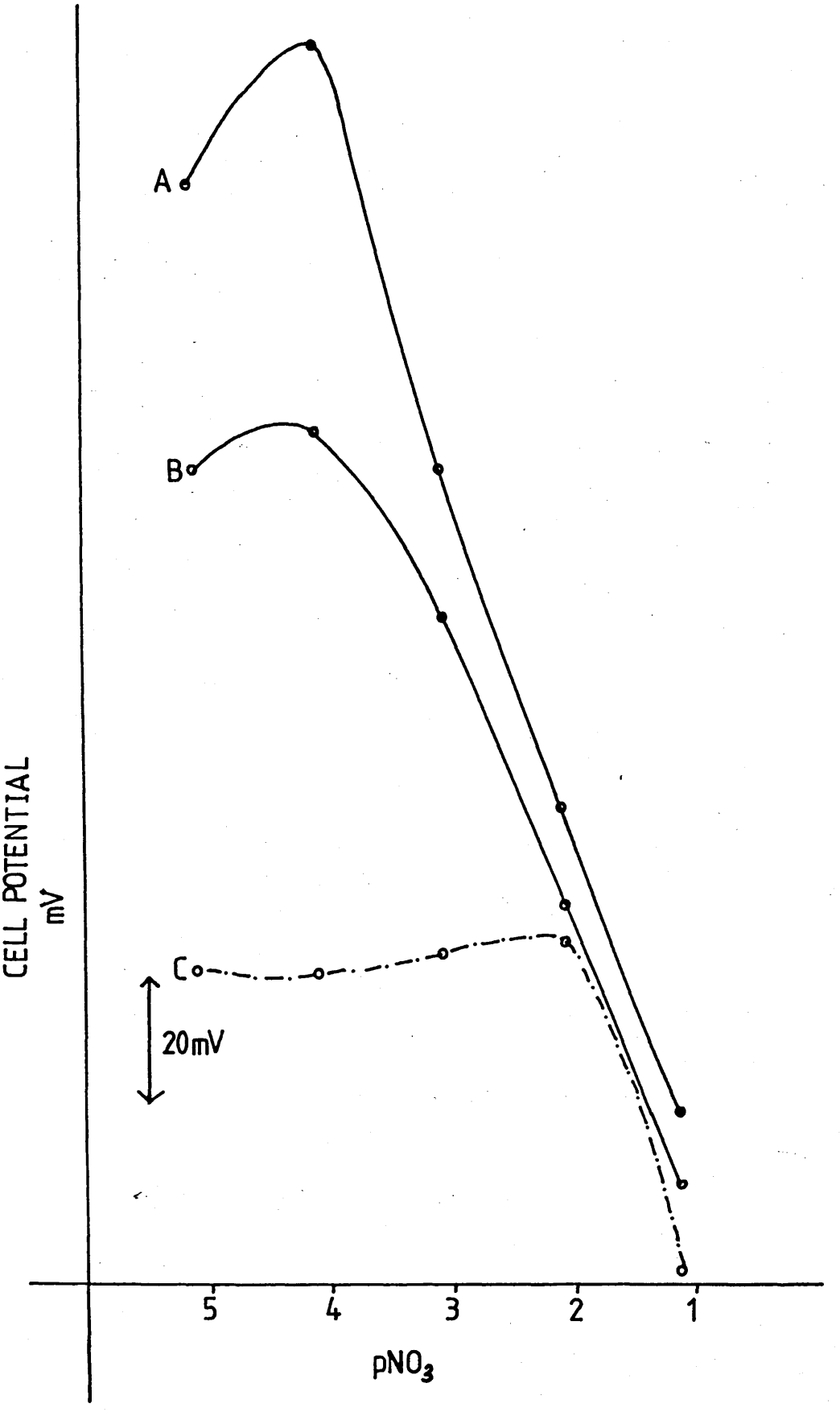


Fig.4.3
The response of electrode M1 to solutions with 10^{-3} mol dm^{-3} interferent ions

A. SO_4^{2-}
B. Cl^-
C. OH^-

the mixed solution method described in Section 3.1.3.1 with 10^{-3}mol.cm^{-3} of interferent ion. The membranes all showed severe interference in the presence of hydroxide ion, a typical response is shown in Figure 4.3. The interference from chloride and sulphate ions was generally less severe. The selectivity coefficient $k_{NO_3\ Cl} = 1.4 \times 10^{-1}$ (mixed solution method, 10^{-3} mol dm^{-3} interferent), for sensor unit M1 prepared from the master membrane D3 was compared with $k_{NO_3Cl} = 10^{-2}$ for the Philips IS561 - NO_3^- plastic membrane electrode (determined in 10^{-1} mol dm^{-3} pure solutions by the separate solution method).

The inhomogeneous appearance of the master membranes and the variability of their response to nitrate was thought to be caused by uneven distribution of cross-linked QAS. The QAS was not evenly incorporated into the polymer matrix, and areas of precipitation were observed in several membranes. The cross-linking of QAS may also be uneven in areas which appear otherwise homogeneous. The response of all the electrodes was less than the expected Nernstian response of -59.2mV per decade change in nitrate activity. The linear response of commercial nitrate electrodes extends to 10^{-5}mol dm^{-3} whereas the best of the above electrodes only extended to 10^{-3}mol dm^{-3}.

In order to improve the response and extend the linear range of the electrodes a new series of membranes was prepared with higher percentages of QAS. The incorporation

of higher levels of QAS was expected to increase the number of sensor units in the cross-linked polymer and improve the sensitivity of the electrodes, thus improving the slope and extending the linear range. These membranes were prepared in the modified casting apparatus described in Section 2.3.2.1b. The casting apparatus was used in an attempt to produce more homogeneous polymers. The electroanalytical properties of the master membranes were evaluated using a Philips 1S561-NO_3 electrode body as described in Section 3.2.1.4.

The electrode body Plate 3.1 was modifed to expose a larger area of membrane to the test solution. The sensor units had a surface area of 64 mm^2, the electrode body exposed only 10 mm^2. The decrease in area and the robust nature of the membrane caused poor response. The membranes were too inelastic to form a hemispherical surface in the membrane cavity. The electrode body was designed for PVC membranes which are soft and flexible. Air bubbles became trapped in the vacant cavity at the membrane surface, interrupting or interfering with the response. An adaptor was designed which exposed a 28mm^2 area of membrane. The size of the cavity and the tension within the electrode were sufficient to form the desirable hemispherical surface and prevent air bubbles gathering at the membrane surface. Conditioned membranes were rinsed, blotted dry and placed in

the electrode assembly. The membranes were held in place by the spring tension within the electrode body, which formed a water-tight seal between the electrode body and membrane.

4.2 Solvent Cast Membranes with Increased Quaternary Ammonium Salt.

The series of membranes prepared by the solvent casting method using higher percentages of QAS are listed in Tables 2.6 and 2.7. The membranes were prepared using 5-12% W/W QAS/SBS and the modified casting apparatus. The new arrangement of smaller casting rings produced more homogeneous membranes when low percentages of QAS were used, but precipitation was evident in those membranes prepared with high percentages of QAS. The membranes were conditioned and examined using the commercial electrode body, as described previously. This series of membranes were more variable in response, and their properties were generally poorer in terms of slope and range than the original solvent cast membrane M6 produced the most consistent response although within this group membrane M6B deteriorated very rapidly (Figure 4.4).

The series of membranes prepared as variations of the M6 membrane formulation showed similar properties to M6, the membranes showed good response down to 10^{-3}mol dm^{-3} but deterioration in slope occurred in more dilute solutions. No improvement on the master membrane M6 was found in these formulations. The electroanalytical properties of the membranes are summarised in Table 4.2.

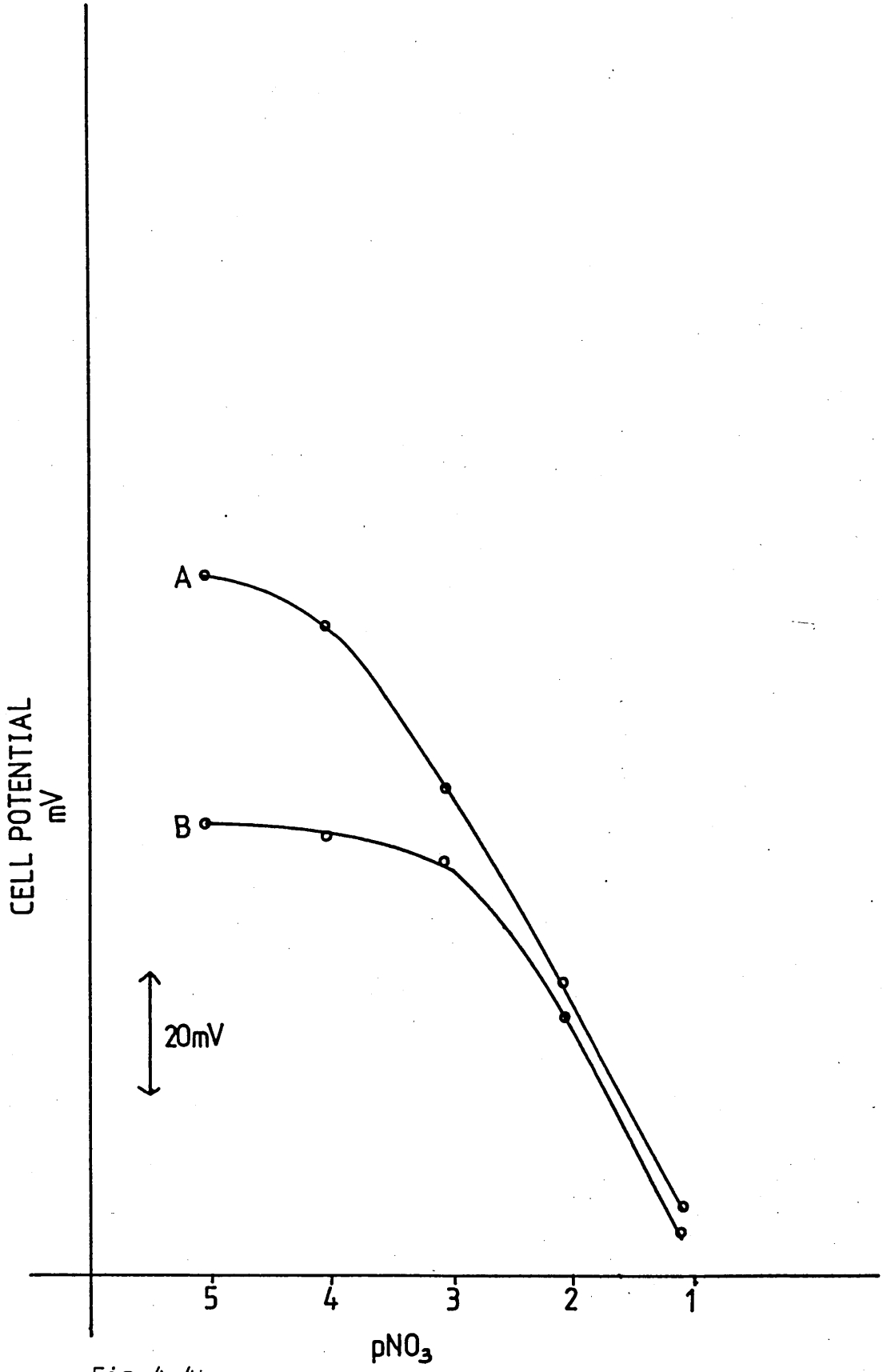


Fig.4.4
The response of master membrane M6B.
A. 1st Calibration (1 day in conditioning solution)
B. 2nd Calibration (2 days in conditioning solution)
(Solutions buffered with potassium dihydrogen orthophosphate 10^{-2}mol dm^{-3}).

TABLE 4.2

Electroanalytical Properties of Solvent Cast Membranes with Increased Quaternary Ammonium Salt.

Master Membrane	Sensor Unit	Linear Range (approximate) (mol dm^{-3})	Slope (mV)	Age[a] (days)	QAS	% W/W QAS/SBS	Resistance (ohms) Unconditioned	Conditioned
1	M1A	Not Linear	-10	2	DADEAB	10.82	$1.7\text{-}7.0\times10^{9}$	1.9×10^{6}
2	M2A	$10^{-1}\text{-}10^{-2}$	-35	2	DADEAB	6.81	$1.5\text{-}6.0\times10^{10}$	1.7×10^{6}
3	VERY ERRATIC AND POOR RESPONSE				DADEAB	12.17	-	-
5	M5A	$10^{-1}\text{-}10^{-3}$	-38	1	TABAB	7.57	$1.6\text{-}2.2\times10^{-8}$	2.3×10^{8}
	M5A A	$10^{-1}\text{-}10^{-3}$	-37	6			-	-
6	M6 1	$10^{-1}\text{-}10^{-3}$ extends 10^{-4}	-51 -30	30	TABAB	7.83	$3.1\text{-}5.0\times10^{9}$	2.6×10^{7} -3.4×10^{8}
	M6 B	$10^{-1}\text{-}10^{-3}$	-35	1				-
		$10^{-1}\text{-}10^{-2}$	-34	2				
		$10^{-2}\text{-}10^{-3}$	-25	2				
	M6 A	$10^{-1}\text{-}10^{-3}$	-52	11				$1.2\text{-}2.6\times10^{7}$
7	M7 A	NO RESPONSE			TABAB	5.14	$2.5\text{-}5.0\times10^{10}$	3.9×10^{7}
8	M8 A	$10^{-1}\text{-}10^{-3}$	-27	2	TABAB	10.76	1.5×10^{8}	$3.8\text{-}6.0\times10^{10}$
		$10^{-1}\text{-}10^{-2}$	-56	9			-1.7×10^{9}	
		$10^{-2}\text{-}10^{-3}$	-33					
		$10^{-1}\text{-}10^{-2}$	-50	15				

ABL . continue

9	M9 A	10^{-1}-10^{-2} 10^{-2}-10^{-3}	-58 -39	5	TAEAB	8.08	8.2×10^{9} 6.0×10^{10}	-
M1JAN	M1JAN	10^{-1}-10^{-2} 10^{-2}-10^{-3}	-53 -41		TAPAB	8.00	$1.1\text{-}3.6\times10^{10}$	3.7×10^{10}
MFEB1	A1 B1 C1	10^{-1}-10^{-3} - 10^{-1}-10^{-3} 10^{-3}-10^{-4}	-29 - -36 -30	3 - 3	TABAB	7.97	3.0×10^{7} 3.5×10^{-7} 10^{10}	1.0^{10}-10^{11} 10^{9} 10^{10}
MFEB3	B1	10^{-1}-10^{-3} Deteriorates to very poor response after 5 days	-58		TABAB	8.03	-	10^{9}-10^{10}

a Number of days in conditioning solution

All solutions were buffered with 10^{-2} mol dm^{-3} potassium dihydrogen orthophosphate.

The resistance of the membranes was measured using several pieces of unconditioned and one conditioned membrane. The conditioned resistance was generally lower than the unconditioned resistance due to the presence of water. The membranes became opaque during conditioning due to the uptake of water; SBS is known to swell slightly in water. There was an increase in resistance of some membranes after conditioning and calibration probably because of QAS leaching from the membranes. The QAS are thought to form a conductive network within the membrane, their removal would increase the resistance. Polymer membranes prepared from SBS without QAS show resistances in excess of 10^{12}ohms, when conditioned.

Increasing the QAS levels in the membranes caused deterioration in the properties of the membranes as nitrate sensors, and generally deterioration in the quality of the polymers. The problem was attributed to the incompatibility of the components of the membrane, SBS is insoluble in methanol, the QAS are soluble only in methanol and water. When small quantities of QAS were used with only minimal amounts of methanol ($<1cm^3$) homogeneous dispersion or emulsions of the two solutions occurred. Increasing the level of QAS in the polymer resulted in more methanol being required to form the QAS solution ($<2cm^3$), and more concentrated solutions of QAS

were added to the SBS/THF solution. However the QAS did not remain in solution during solvent casting. The QAS precipitated from the solution, the problem increased with higher percentages of QAS. It seems possible that when large quantities of QAS are included in the polymers, their precipitation occurs rapidly, and prevents reaction with the polymer to form a covalently bound sensor. This would account for the lack of response or deterioration of several membranes. The extent of covalent attachment of QAS is probably limited by the rate of precipitation. Therefore if more QAS is required to achieve Nernstian response or linear response over an extended range, then an alternative method of membrane preparation is required which eliminates the problem of incompatibility in the curing solution.

4.3 Hot Pressed Membranes

The method chosen for this work which is used frequently in polymer processing, was hot-pressing. The experimental details are outlined in Section 2.3.2.2. Polymer solutions were freeze dried to produce a crumb, fibre, or film which was then pressed between heated dies to form a polymer membrane. The membranes prepared by this method are listed in Table 2.8 and their electroanalytical properties are summarised in Table 4.3. Membranes prepared by this method were even in texture (with the exception of some gas bubbles) firm, flexible and tough although some membranes

TABLE 4.3

Electroanalytical Properties of Hot Pressed Membranes

Master Membrane	Sensor Unit	Linear Range	Slope (mV)	Age[a] (days)	QAS	% W/W QAS/SBS
HPA	HPA1	10^{-1}-10^{-3}	-44	1 day	DADMAC	2.66
	HPA2	10^{-1}-10^{-3}	-40			
		NON LINEAR	-	4		
HPB	HPB1	10^{-1}-10^{-2}	-58	1	TAEAB	1.82
		10^{-2}-10^{-3}	-34			
		10^{-1}-10^{-2}	-41	10		
		10^{-2}-10^{-3}	-20			
HPC	HPC1	10^{-1}-10^{-5} (APPROX)	-30	1	DADMAC	2.30
		NON LINEAR	-15	1 (2nd Test)		
HP(ABIN)	HP(ABIN)1	10^{-1}-10^{-3}	-40	1	TAEAB	1,90
		NON LINEAR	- 10	1 (2nd Test)		

[a] Number of days in conditioning solution

All solutions were buffered with 10^{-2} mol dm^{-3} potassium dihydrogen orthophosphate.

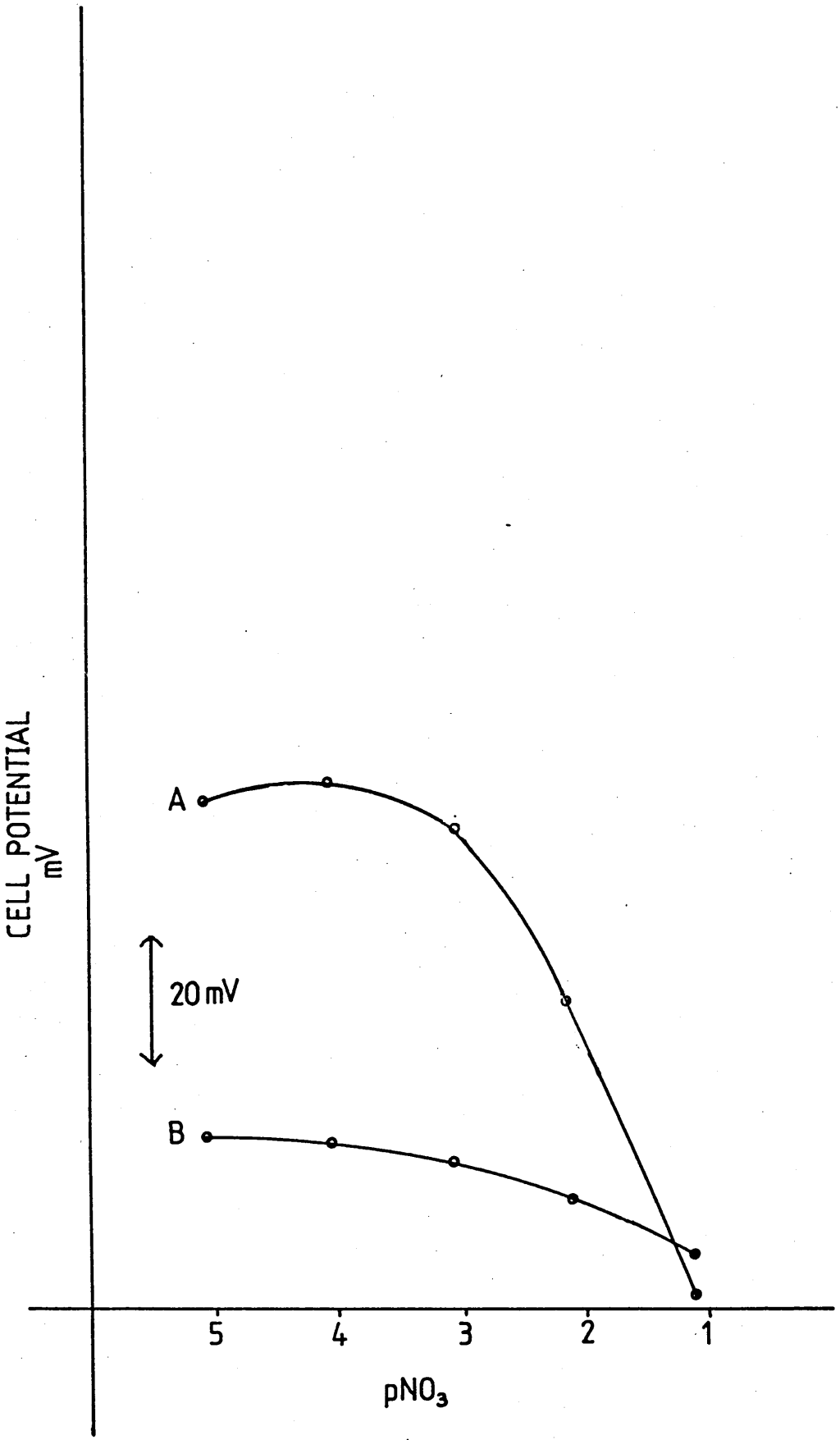


Fig.4.5
The response of electrode HP(ABIN)1.
A. 1st Calibration (24 hours conditioning)
B. 2nd Calibration (48 hours conditioning)
(Buffered Standards 10^{-2} mol dm^{-3} potassium dihydroge orthophosphate).

were not cross-linked. The bubbles trapped within the polymer were caused by insufficient pressure, or the production of gaseous nitrogen from the initiator ABIN.

The conditioned membranes were found to show only moderate response to nitrate in concentrated, buffered solutions, with poor response to dilute solutions. The membranes all showed rapid deterioration in response within hours or days of conditioning and the initial calibration. The very rapid deterioration was thought to be caused by leaching of QAS from the polymer. This was not unexpected for membranes which were not cross-linked, but the deterioration also occurred with the cross-linked membrane HP(ABIN). The response of this master membranes is shown in Figure 4.5 and is typical of the hot-pressed membranes.

This method of membrane preparation did not appear to eliminate the problem caused by incompatibility of the membrane components. Although cross-linked membranes were obtained, the cross-linked matrix appeared to contain negligible amounts of covalently bound QAS, and the response of the membranes to nitrate was poor.

4.4 Membranes Prepared with tert-Butylhydroperoxide (tBHP) Initiator

The preparation of cross-linked membranes by solvent casting was reasonably successful, but the incompatability of the solution of QAS and polymer prevented any further development of these polymers. A new method of membrane preparation was required which was suitable for covalent

attachment of large amounts of QAS to the polymer SBS, without separation of the two component solution during the reaction. The initiator tBHP was used by Butler[85-92] and co-workers to polymerise QAS with allyl substituents. When tBHP was used in this work to prepare oven cured, SBS membranes no cross-linking was observed with 1.9% W/W (0.0483g tBHP) and 4.4% W/W (0.1101g tBHP) but a cross-linked membrane was obtained when 10.3% W/W (0.2561g tBHP) was used. Therefore tBHP was expected to act preferentially on the allyl unsaturation and promote extensive attachment of the QAS to the SBS polymer. The extent of butadiene-butadiene cross-linking was expected to be minimal with the levels of tBHP used in the polymers.

The membranes prepared by solvent casting in an oven at 60°C with tBHP initiator, are listed in Table 2.9; the method of preparation is outlined in Section 2.3.2.3. The membranes were cross-linked and superior in appearance to any previous membranes. There was no evidence of precipitation and several of the membranes were completely transparent, and others, though cloudy were homogeneous. The membranes were conditioned in the usual way and their response to nitrate was evaluated using the Philips IS 561 electrode body with the 'inhouse' extension, Section 3.2.1.4. The master membranes tBHPA - tBHPF (Table 2.9) showed little or no response to nitrate, with slopes of 5-10 mV change in cell potential over 4 decades. The membranes were conditioned

for several weeks and re-examined at intervals to ensure that conditioning time was not the limitation on response.

The membranes tBHPHand tBHPG (Table 2.9) were prepared using relatively large amounts of QAS and low levels of initiator compared to the membranes tBHPA-tBHPF. These two membranes showed good response to nitrate. They were both cross-linked, but tBHPH was even and homogeneous, tBHPG was greasy and less homogeneous. The quality of tBHPG was probably affected by the very hygroscopic QAS, DADEAC, used in its preparation.

The master membrane tBHPH showed consistent response to nitrate for all pieces of the membrane examined, regardless of the side of the membrane exposed to the test solution. The calibration curve A in Figure 4.6 is typical of the response obtained from the tBHPH membranes. The membranes showed Nernstian response from 10^{-1} to 10^{-3} mol dm^{-3} and sub-Nernstian response to 10^{-4} mol dm^{-3}, for unbuffered solutions. The response times of the membranes were very fast (10-15s) in the more concentrated solutions (10^{-1} to 10^{-3} mol dm^{-3}) becoming slower (15-30s) in more dilute solutions (10^{-4} and 10^{-5} mol dm^{-3}), Figure 4.7. These response times followed the same pattern as those observed for the most successful sensor unit M1, prepared from master membrane D3, Section 4.1. The selectivity of the tBHP membranes for nitrate in the presence of other ions was poor. Although the membranes responded in almost Nernstian fashion, down to 10^{-4} mol dm^{-3},

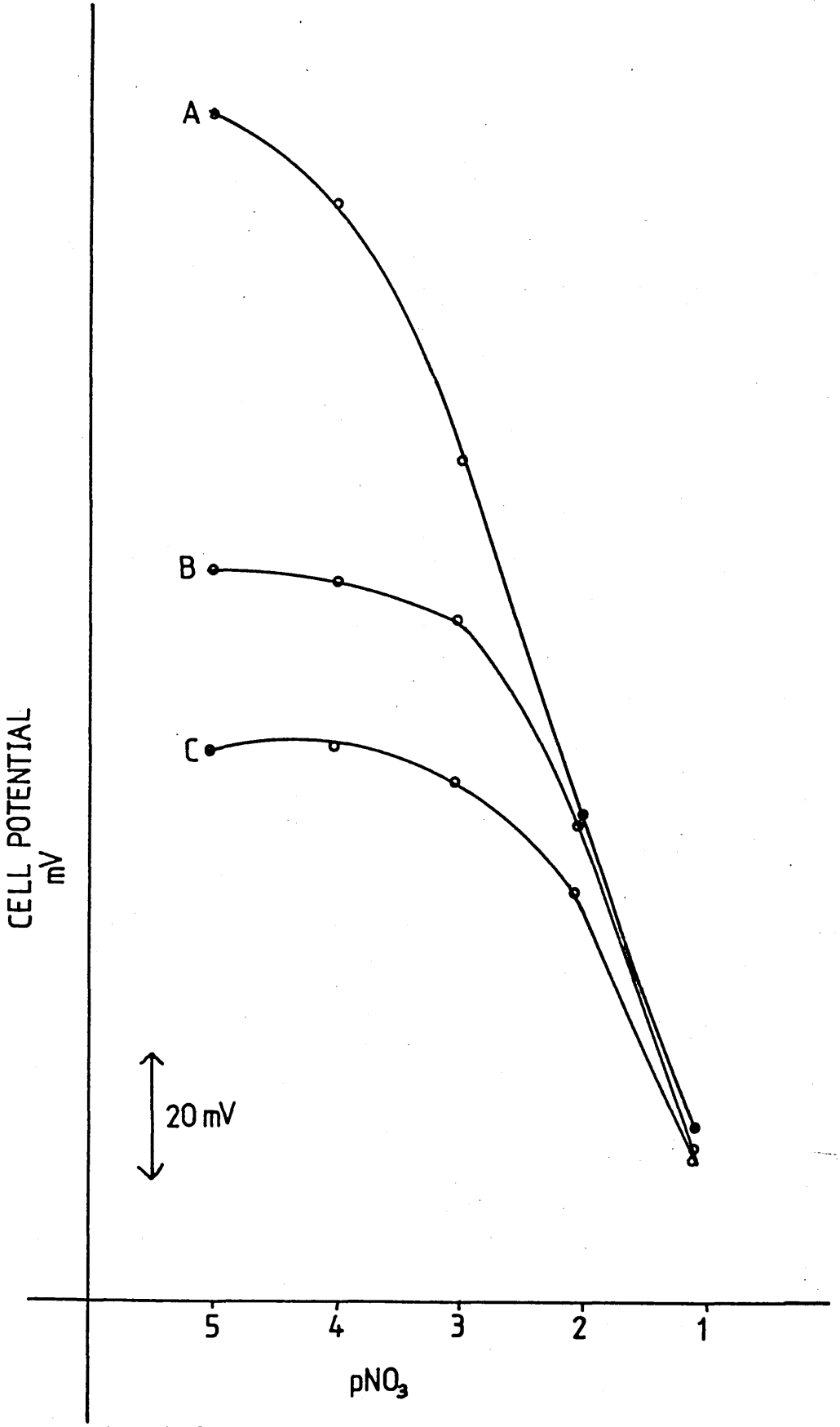


Fig.4.6
The response of master membrane t8HPH in the presence of 10^{-2}mol dm^{-3} potassium dihydrogen orthophosphate buffer (B). 10^{-2}mol dm^{-3} chloride (C) interferant compared to the response of the membrane to nitrate standards (A).

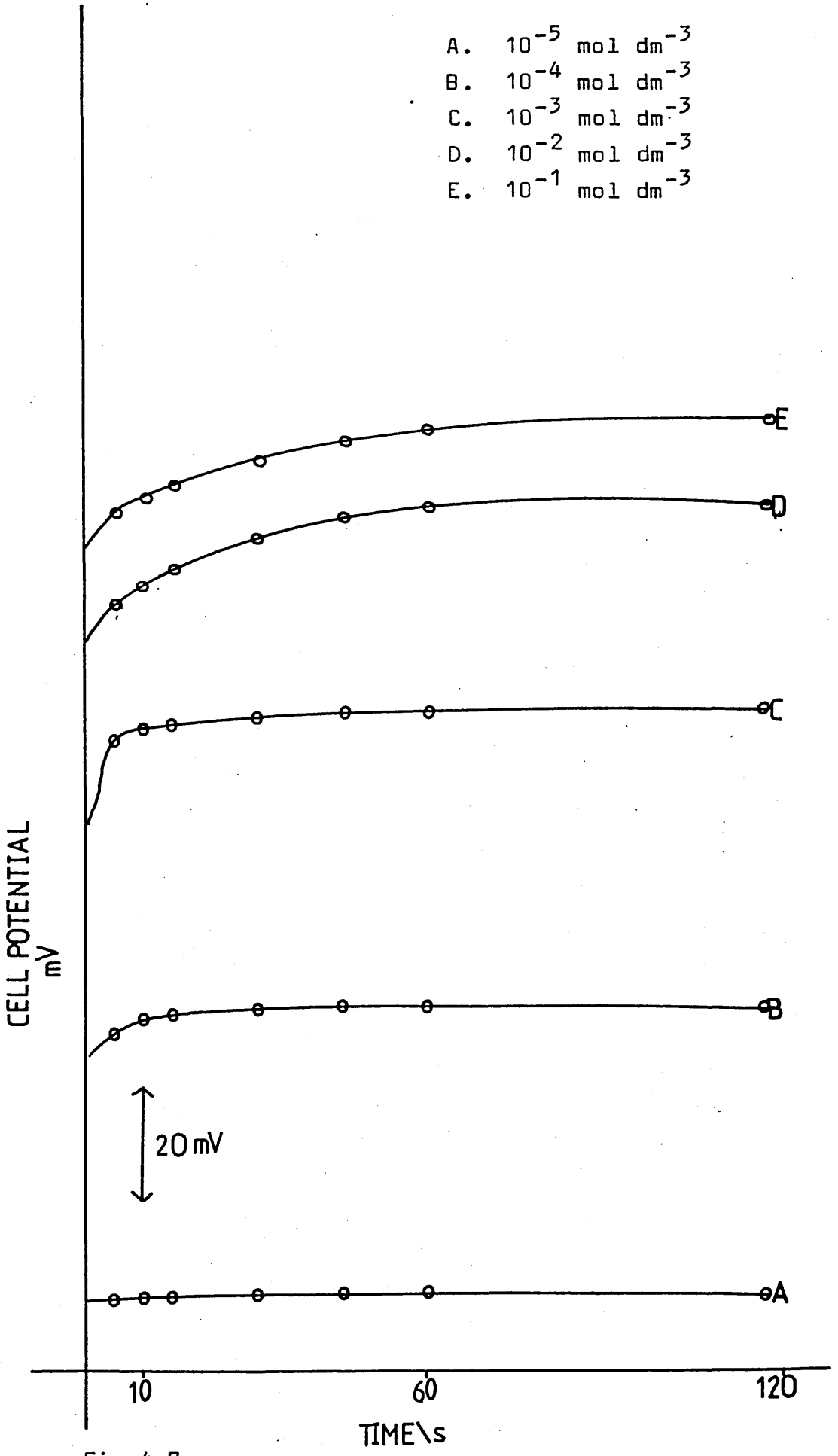


Fig.4.7
The response time of membrane tBHPH2 in unbuffered KNO_3 standards.

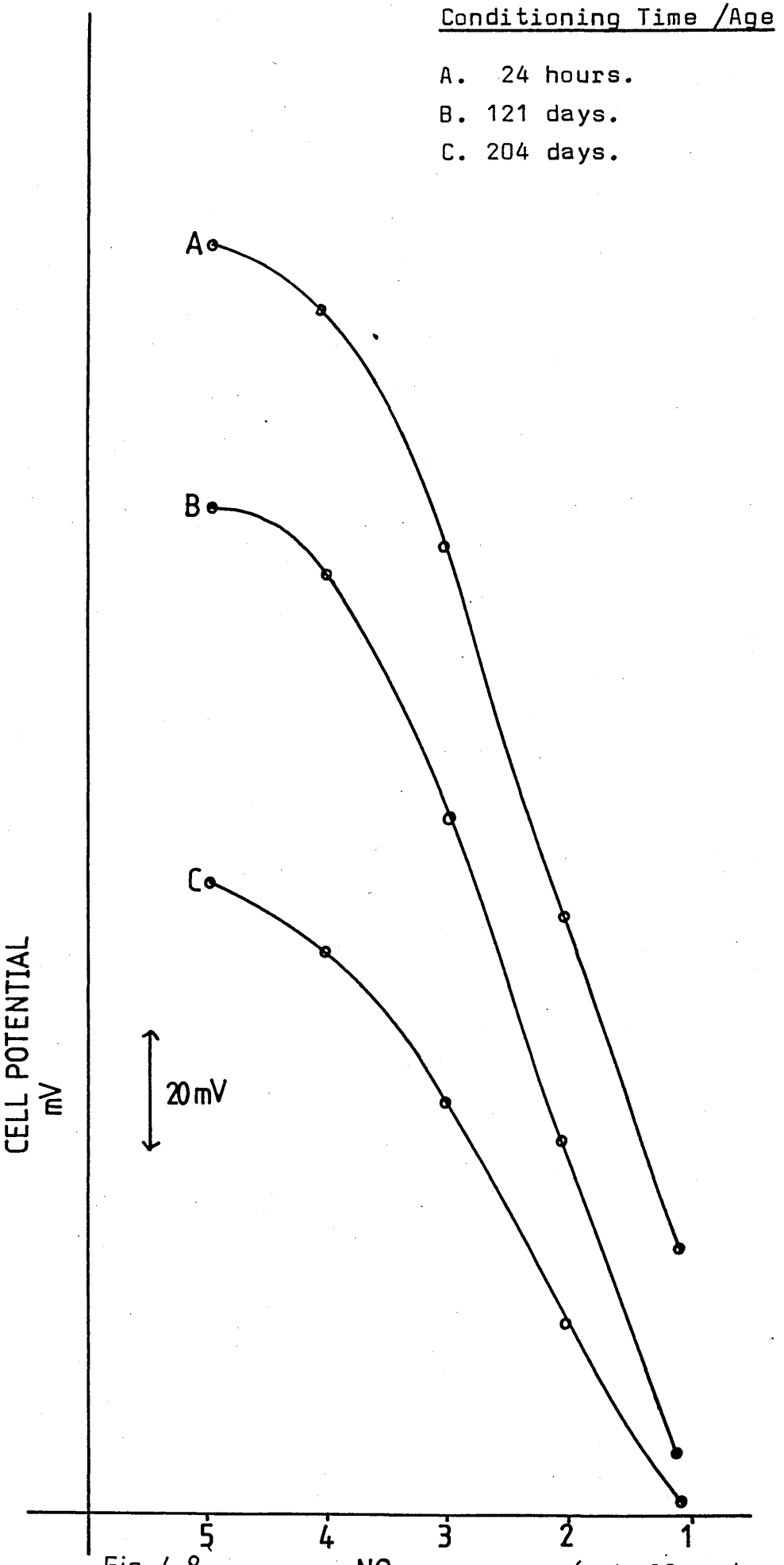


Fig. 4.8
The response of tBHPH membranes at various ages.

in unbuffered solution in the presence of 10^{-2} mol dm^{-3} buffer the response was Nernstian to 10^{-2} mol dm^{-3} levelling off at 10^{-3} mol dm^{-3}, Figure 4.6. The membranes are strongly interfered with by chloride and sulphate ions, Figure 4.6. The lifetime of the tBHPH membranes was very encouraging. Selected membranes, stored in conditioning solution, were examined at intervals over several months Figure 4.8. Slight deterioration in the response of the membrane tBHPH was observed 121 days after the initial conditioning. The slope of the calibration for the membrane tBHPH was still 30-40mV per decade for 10^{-1}- 10^{-3} mol dm^{-3} solutions, 204 days after the initial conditioning.

The master membrane tBHPH was the most successful of this series of membranes and comparable to the sensor unit M1 in terms of lifetime, response time and range, although it appeared to be less selective. However the major advantage of using tBHP initiator and this method of membrane preparation was the homogeneous nature of the polymer membranes and their consistent electroanalytical properties. Solvent casting produced several useful electrodes but reproducibility within master membranes and between master membranes was not observed. The formulation of master membrane tBHPH was repeated, and the second membrane showed consistent electroanalytical properties identical to the original membrane. Both membranes are referred to as tBHPH.

The formula was varied slightly to examine the influence of QAS and initiator on the electroanalytical properties. The master membranes MAY6 to MAY10, Table 2.10 were prepared with higher levels of QAS and initiator, than the original tBHPH master membrane. The membranes were all homogeneous and cross-linked. Incorporating extra QAS into the polymer did not have a significant effect on the response of the membranes to unbuffered nitrate solutions. The response of these master membranes was almost identical to that of tBHPH in terms of speed of response and range. However the master membrane MAY10 appeared to suffer less interference in the presence of 10^{-2} mol dm^{-3} chloride ion (Figure 4.9) than the original tBHPH membrane (Figure 4.6). Incorporating higher levels of QAS into the polymers may also increase their useful lifetimes if this is limited by decomposition of the polymer structure. The conditioning time of master membrane MAY10 was examined and found to be quite rapid, Figure 4.10.

The properties of all membranes prepared with tBHP initiator were examined in detail in an attempt to highlight the qualities of the polymer membrane which produced successful nitrate electrodes. The results of Kjeldahl analysis, cross-linked density measurements and the resistance of conditioned and unconditioned membranes tBHPA-tBHPH are shown in Table 4.4. The amount of quaternary nitrogen

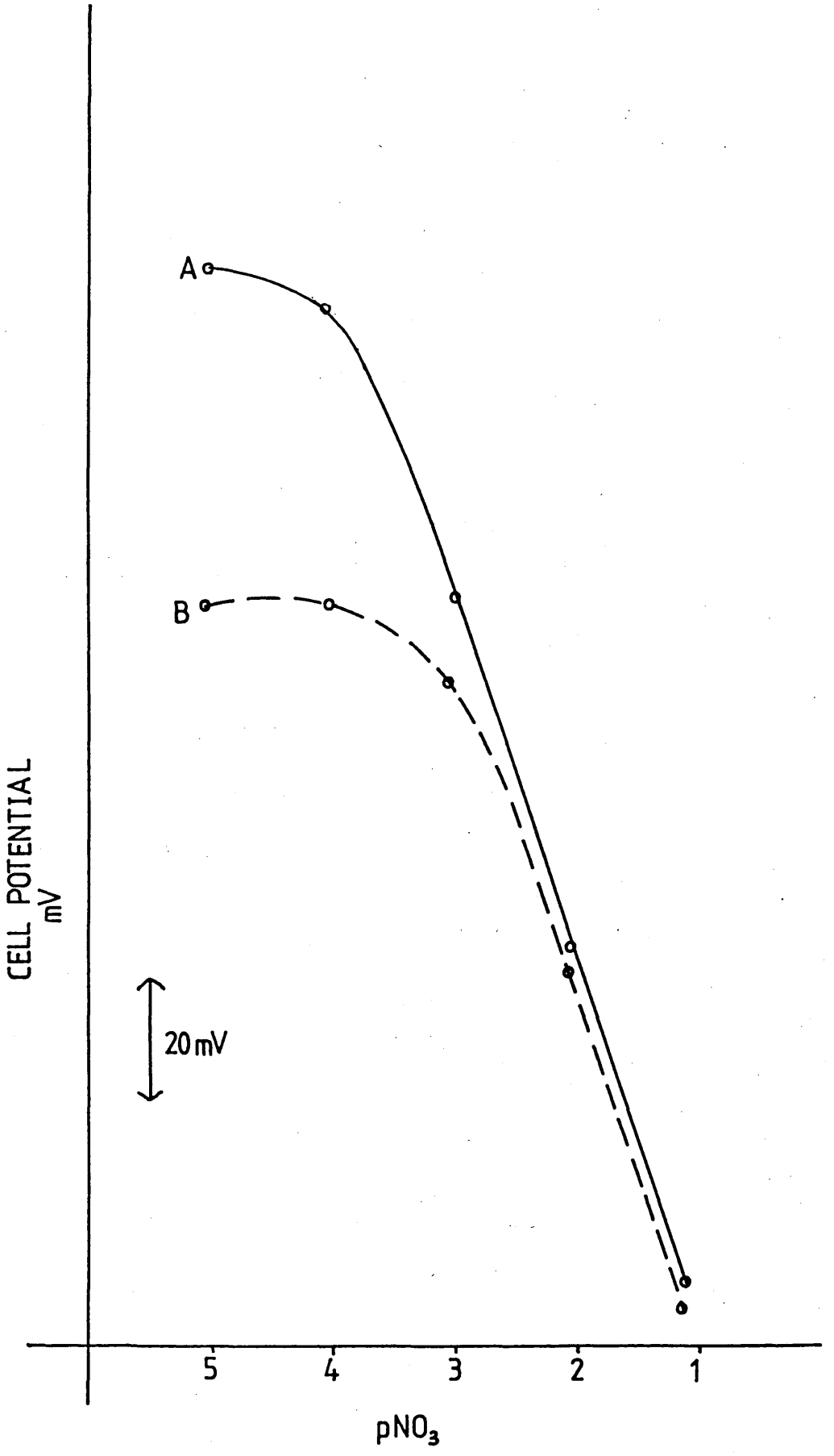


Fig.4.9
The response of master membrane MAY10 to unbuffered nitrate standards (A) and nitrate standards with 10^{-2} mol dm^{-3} chloride interferent (B).

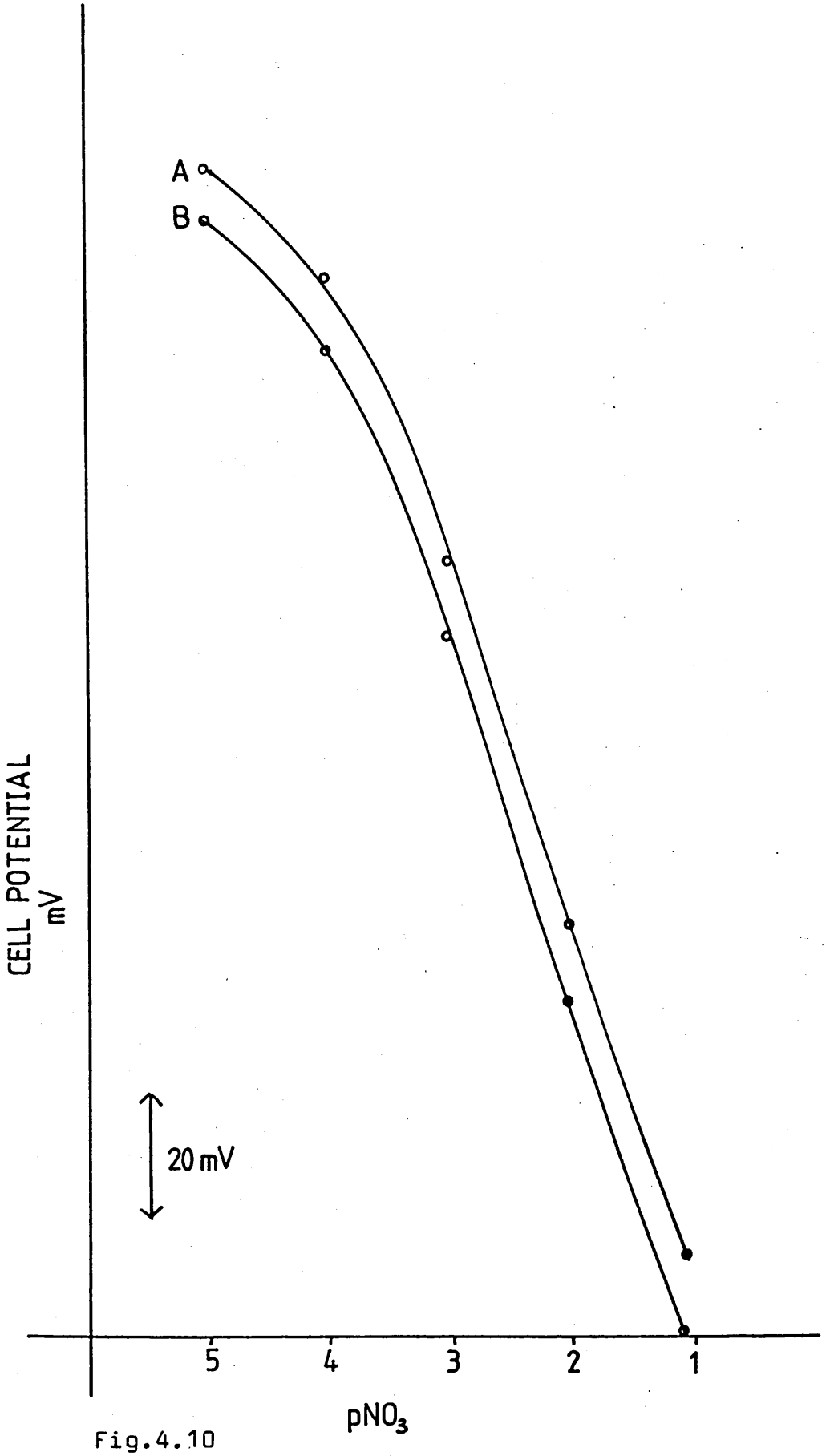


Fig.4.10
The response of master membrane MAY10 after 6 hours (A) and 24 hours (B) conditioning.(Unbuffered Solutions).

Properties of the Membranes Prepared using tBHP as Initiator

Master Membrane	Type [c]	QAS % W/W [a]	% Nitrogen W/W (Kjeldahl Analysis) [d]		% Nitrogen W/W (Expected)	Cross-linked Density Moles Cross-links cm^{-3}	Resistance (Ohm Unconditioned	Cond
A	TAAB	3.96	C 0.10 I 0.29 E 0.10		0.21	4.26×10^{-5}	3.5×10^{9}	$3.2 \times$
B	TAAB	4.13	C 0.14 I 0.09 E 0.49	0.06 0.06 0.15	0.22	8.54×10^{-4}	5.6×10^{9}	$3.4 \times$
C	DADMAC	4.24	C 0.07 I 0.37 E 0.31		0.35	8.82×10^{-5}	5.4×10^{9}	$1.0 \times$
D	TAMAB	4.04	C 0.26 I 0.62 E 0.23	I 0.20 [b] I 0.38 E 0.06	0.23	7.34×10^{-5}	6.0×10^{9}	$4.7 \times$
E	TAAB	4.21	C 0.05 I 0.15 E 0.16		0.22	9.68×10^{-5}	6.2×10^{9}	$4.5 \times$
F	TAAB	4.00	C 0.17 I 0.08 E 0.59		0.21	5.28×10^{-4}	4.6×10^{9}	$2.1 \times$
G	DADEAC	11.79	E { 0.51 0.67 0.49		0.79	7.98×10^{-6}	2.0×10^{6}	$2.8 \times$
H	TAEAB	10.16	C 0.53 I 0.50 E 0.66	I 0.25 [b] I 0.30 E 0.24	0.52	7.38×10^{-6}	3.0×10^{7}	$2.0 \times$

a % W/W QAS/SBS. b 24 hours Extraction

c TAAB Tetraallylammonium Bromide
DADMAC Diallyldimethylammonium Chloride
DADEAC Diallyldiethylammonium Chloride
TAEAB Triallylethylammonium Bromide

d C - Central area of membrane
I - Intermediate area of membrane
E - Edge of membrane.

covalently bound to the polymer structure for all the membranes was less than expected. The results from Kjeldahl analysis performed on extracted membranes was representative of covalently bound nitrogen, because entangled QAS was removed by methanol during soxhlet extraction, Section 3.4. The distribution of QAS across the polymer membrane suggested that a chromatographic movement of QAS, to the edge of the polymer, was occurring. The highest levels of QAS were found in the outer area of the polymer for almost all the unextracted samples; comparison with extracted samples of tBHPB, D and H suggested that much of the QAS in this area was not covalently attached to the polymer. This pattern was observed for other membranes prepared with tBHP initiator discussed below and illustrated in Tables 4.5 and 4.6.

The cross-linked densities of the unresponsive membranes tBHPA-tBHPF were one or two orders of magnitude higher than those of membranes tBHPH and tBHPG which showed good response to nitrate. The higher degree of cross-linking is also reflected in the resistance of conditioned and unconditioned membranes. The resistance of the membranes was not reduced by conditioning, which suggested that very little absorption of water had occurred; possibly because of the high degree of cross-linking. Membranes tBHPA-D were prepared with approximately five times the amount of initiator as tBHPG and tBHPH and one half or one third of the QAS used in the last two membranes. The difference in response of the

TABLE 4.5

Properties of the Membranes Prepared using TAEAB and tBHP as Initiator

Master Membrane	% W/W[a] TAEAB	tBHP (g)	% Nitrogen W/W (Kjeldahl Analysis)[d]		% Nitrogen W/W (Expected)	Cross-linked density (Moles cross-links cm^3)	Resistance (O	
				After Extraction			Unconditioned	Condi
1 H	10.16	0.0192	C 0.53 I 0.50 E 0.66	I 0.25 I 0.30 E 0.24	0.52	7.38×10^{-6}	3.0×10^{7}	2.0
(REPEAT) H	10.16	0.0190	C 0.43 I 0.38 E 0.43	C 0.26 I 0.29 E 0.31	0.52	1.02×10^{-5}	-	
MAY8	14.81	0.0634		C 0.37 I 0.26 E 0.65	0.74	5.2×10^{-6}	5.0×10^{9}	10^{11}
MAY9	15.00	0.1102		C 0.38 I 0.68 E 0.37	0.74	1.07×10^{-5}	3.5×10^{11}	6 x
MAY10	10.21	0.1085		C 0.29 I 0.54 E 0.30	0.53	1.04×10^{-5}	7.5×10^{11}	4.5

For footnotes - see Table 4.4

TABLE 4.6

Properties of the Membranes Prepared Using a Range of QAS

Master Membrane	QAS Type[c]	QAS % W/W[a]	% Nitrogen W/W (Kjeldahl Analysis)[b]	% Nitrogen W/W (Expected)	Cross-linked Density (moles Cross-links cm^{-3})	Resistance (Ohms Unconditioned	Resistance (Ohms Condi
JUNE 1	TAAB	10.63	C 0.33 I 0.31 E 0.20	0.52	1.08×10^{-5}	7.0×10^{10}	5 x 1
JUNE 2	TAAB	7.80			3.66×10^{-6}	0.5×10^{11}	1.2 x
JUNE 3	TABAB	11.44	C 0.30 I 0.34 E 0.50	0.54	2.66×10^{-6}	1.5×10^{11}	1.5 x
JUNE 4	ATEAB	9.21	C 0.65 I 0.46 E 0.38	0.53	1.00×10^{-5}	6.5×10^{7}	1.6 x
JUNE 5	DADPAB	10.74			9.94×10^{-6}	2.0×10^{8}	5 x 1
JUNE 6	TAMAB	9.65			9.92×10^{-6}	6.0×10^{11}	10^{8}-1
JUNE 7	DADEAB	9.72	C 0.44 I 0.52 E 0.46	0.53	1.04×10^{-5}	1.5×10^{10}	8.3 x
JUNE 8	DADEAC	11.88	C 0.08 I 0.52 E 0.09	0.78	1.08×10^{5}	7.0×10^{8}	1 x 1
JUNE 9	TAPAB	10.76			1.34×10^{-6}	1.5×10^{7}	5 x 1

a. % W/W QAS/SBS. b. C - Central area of membrane
E - Edge of Membrane
I - Intermediate area of membrane.

TAAB - Tetra-allylammonium Bromide
TABAB - Triallylbutylammonium Bromide
ATEAB - Allyltriethylammonium Bromide
DADPAB - Diallyldipropylammonium Bromide
TAMAB - Triallylmethylammonium Bromide
DADEAB- Diallyldiethylammonium Bromide
DADEAC- Diallyldiethylammonium Chloride
TAPAB - Triallylpropylammonium Bromide

membranes tBHPA-D and tBHPG and tBHPH is not unexpected when the differences in the properties are considered. The high degree of cross-linking observed for tBHPE and tBHPF, which were prepared with less initiator than tBHPA-D but low amounts of QAS appears to be a contradiction of the pattern. It is possible that excess initiator which is present in tBHPA-D, does not promote more cross-linking once an optimum level has been reached. The optimum level may depend on both the type and amount of QAS, the comparison between the properties of tBHPB and tBHPF appear to follow this pattern. The extensive cross-linking and low levels of QAS for tBHPA-F compared to the more successful membranes tBHPG and tBHPH appeared to be responsible for their poor performance as electrode membranes.

The properties of membranes prepared as variations on the tBHPH formulation are shown in Table 4.5. The membranes prepared with approximately 10% QAS, tBHPH and MAY10 were found to have similar levels of covalently bound nitrogen and cross-linking. Increasing the levels of QAS increased the level of covalently bound nitrogen, as shown in MAY8 and MAY9. The average amount of QAS covalently attached to tBHPH after extraction was 0.28%, 54% of the expected level of 0.52% for MAY8 0.43% or 58% of the expected QAS, for MAY9 64% of the expected QAS, for MAY10 71% of the QAS was incorporated into the polymer. The two membranes MAY8 and

MAY10 were prepared with very similar amounts of QAS but MAY9 was prepared with more initiator and a higher percentage of QAS was found to be covalently attached to the polymer. The membrane MAY10 was prepared with the highest ratio of QAS and initiator. The membranes MAY10 and tBHPH were prepared with almost the same amount of QAS but the ratio of initiator was 9:1. The difference in the amount of covelently bound nitrogen in the two membranes reflects the difference in initiator. The cross-linked density of this series of membranes did not follow the expected pattern, increasing the amount of QAS and initiator did not increase the cross-linked density significantly. The membranes tBHPH(REPEAT), MAY9 and MAY10 showed very similar cross-linked density. However the original tBHPH and MAY9 showed lower cross-linked density. It is possible that for certain ratios of QAS and initiator covalent attachment of QAS to the polymer structure is the predominant reaction, and very little polymer cross-linking may occur. If this type of reaction predominates with high levels of QAS it could explain why an increase in cross-linked density was not observed. The method of measurement becomes more approximate when large amounts of QAS are present in the polymer structure, this is discussed in Chapter 6.

4.4.1 Comparison of Different Quaternary Ammonium Salts as Nitrate Sensors.

The membranes prepared with tBHP, and examined in detail were based on the QAS, TAEAB. The range of QAS described earlier (Section 2.2) were prepared to allow a

study of QAS structure and membrane selectivity. In order to compare the response and selectivity of different QAS to nitrate a range of membranes was prepared using tBHP initiator and solvent casting. The membranes described in Table 4.6 were prepared using the formula for tBHPH, but molar equivalents of each QAS were used to produce an equivalent number of quaternary ammonium centres in each polymer. These membranes were all cross-linked and superior in quality to any prepared by solvent casting, although some were less homogeneous than the membranes prepared with TAEAB, Table 2.10 and tBHPH membranes. The quality of the membrane often reflected the hygroscopic nature of the QAS used in its preparation. The very hygroscopic diallyl QAS produced cloudy and greasy membranes.

The membranes were conditioned and their response to unbuffered nitrate solutions was compared (Figures 4.11 and 4.12). The best response was obtained from master membrane JUNE3 which contained TABAB. The response, Figure 4.12A, was linear and Nernstian from 10^{-1} to 10^{-3} mol dm^{-3} but sub-Nernstian from 10^{-3} to 10^{-4} mol dm^{-3}, it was almost identical to the response of master membranes containing TAEAB QAS. The remaining triallyl QAS showed variable response. The QAS TAMAB showed poor response to nitrate, Figure 4.11C. The QAS, TAPAB, which is between TAEAB and TABAB in the homologous series showed linear response to nitrate (master

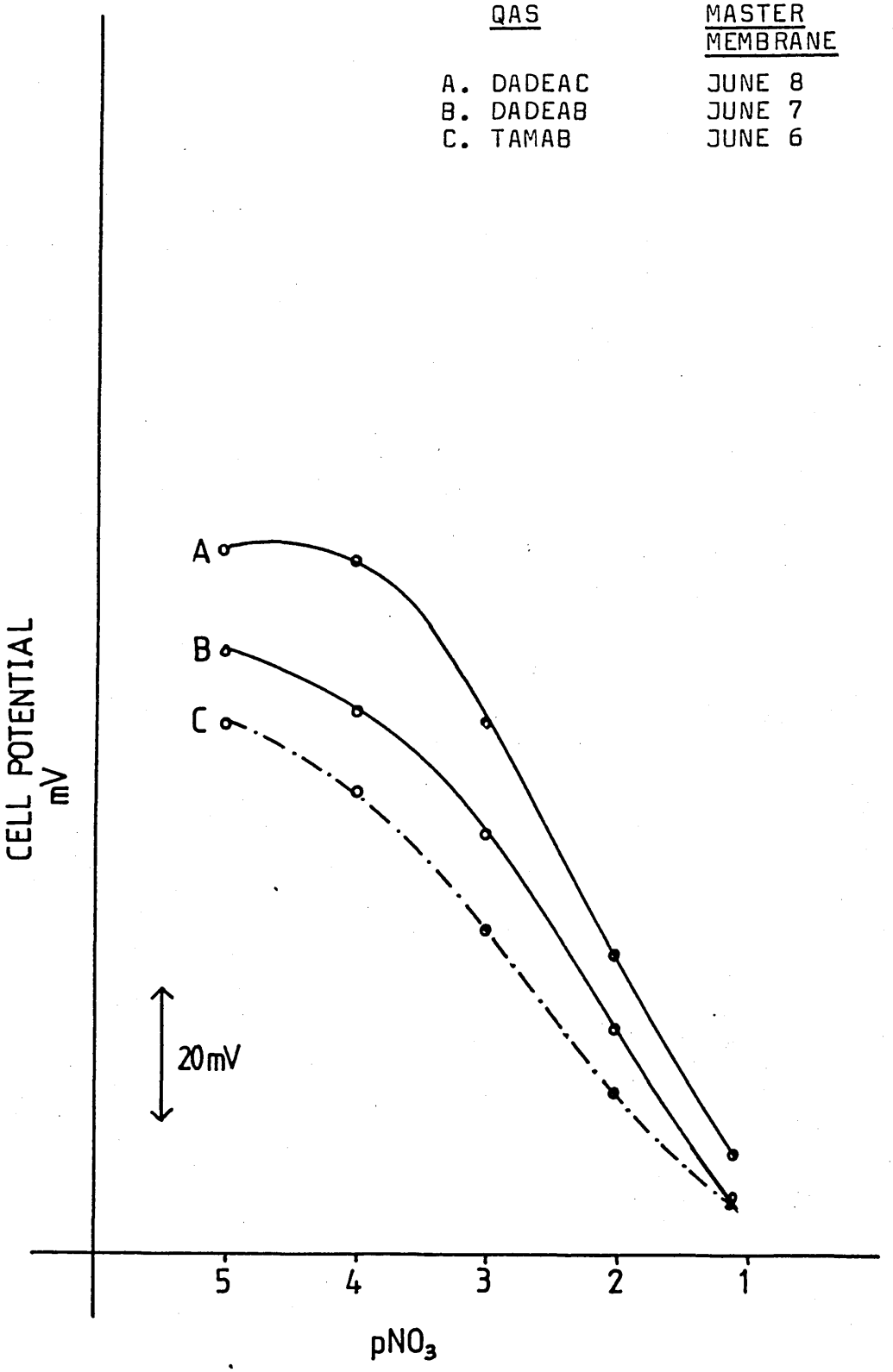


Fig.4.11
The response of master membranes prepared from a range of QAS. (Unbuffered Solutions).

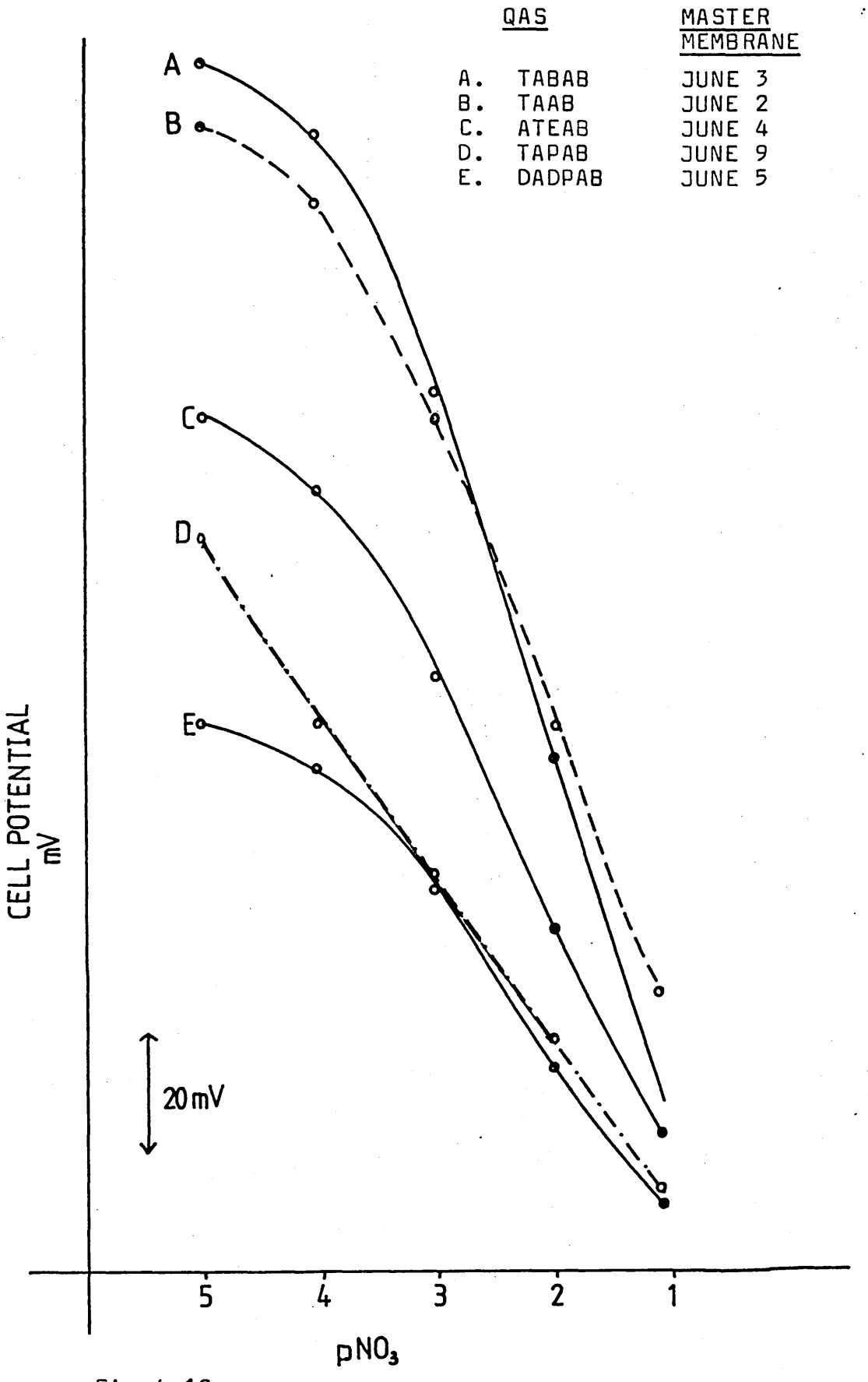


Fig.4.12
The response of master membranes prepared from a range of QAS. (Unbuffered Solutions).

membrane JUNE 9) from 10^{-1} to 10^{-5} mol dm^{-3} with slope of approximately -25mV per decade. The low slope and increase in resistance on conditioning suggested a low level of covalent attachment of QAS. However this was not confirmed by Kjeldahl analysis.

The diallyl QAS, DADEAC, DADEAB and DADPAB all showed similar response to nitrate with low slope and short linear range. The three master membranes prepared with these QAS, JUNE8, JUNE7 and JUNE5 respectively showed very similar levels of cross-linking varying from 9.94×10^{-6} - 1.08×10^{-5} moles cross-links cm^{-3} (Table 4.6). The reactivity of the chloride and bromide QAS during homo-polymerisation is known to be different. The polymerisation of quaternary ammonium chlorides was shown to occur more rapidly[95]. The covalent attachment of QAS to the two master membranes JUNE7 and JUNE8 was evaluated and compared. The quaternary ammonium bromide was evenly distributed across the membrane and a high proportion of the original QAS was covalently bound to the polymer. In comparison the quaternary ammonium chloride was unevenly distributed across the membrane with some areas depleted of QAS.

The monoallyl QAS, ATEAB showed superior response to the diallyl QAS, Figure 4.12C, but this response was erratic and rapid deterioration was observed. The covalent attachment of ATEAB to the polymer is shown in Table 4.6, 94% of the expected QAS was found on analysis.

The tetra-allyl QAS, TAAB showed slightly poorer response to nitrate than TABAB, the response was less reproducible. The most promising QAS was TABAB. The master membrane JUNE3 showed extended linear response to unbuffered nitrate solutions, Figure 4.13, compared to tBHPH. The QAS however showed no superior selectivity for nitrate and the response of the membrane deteriorated in the presence of 10^{-2} mol dm^{-3} buffer. The response of the two membranes at various pH levels was also examined and compared Figure 4.14, the response of both membranes was suppressed at high pH.

A successful method of membrane preparation has been identified along with those properties of polymer membranes which are indicative of useful nitrate response. A range of QAS was examined but no selectivity for nitrate was found although wide variation in the response to nitrate was experienced. The QAS, TAEAB and TABAB, showed superior response to nitrate but poor selectivity.

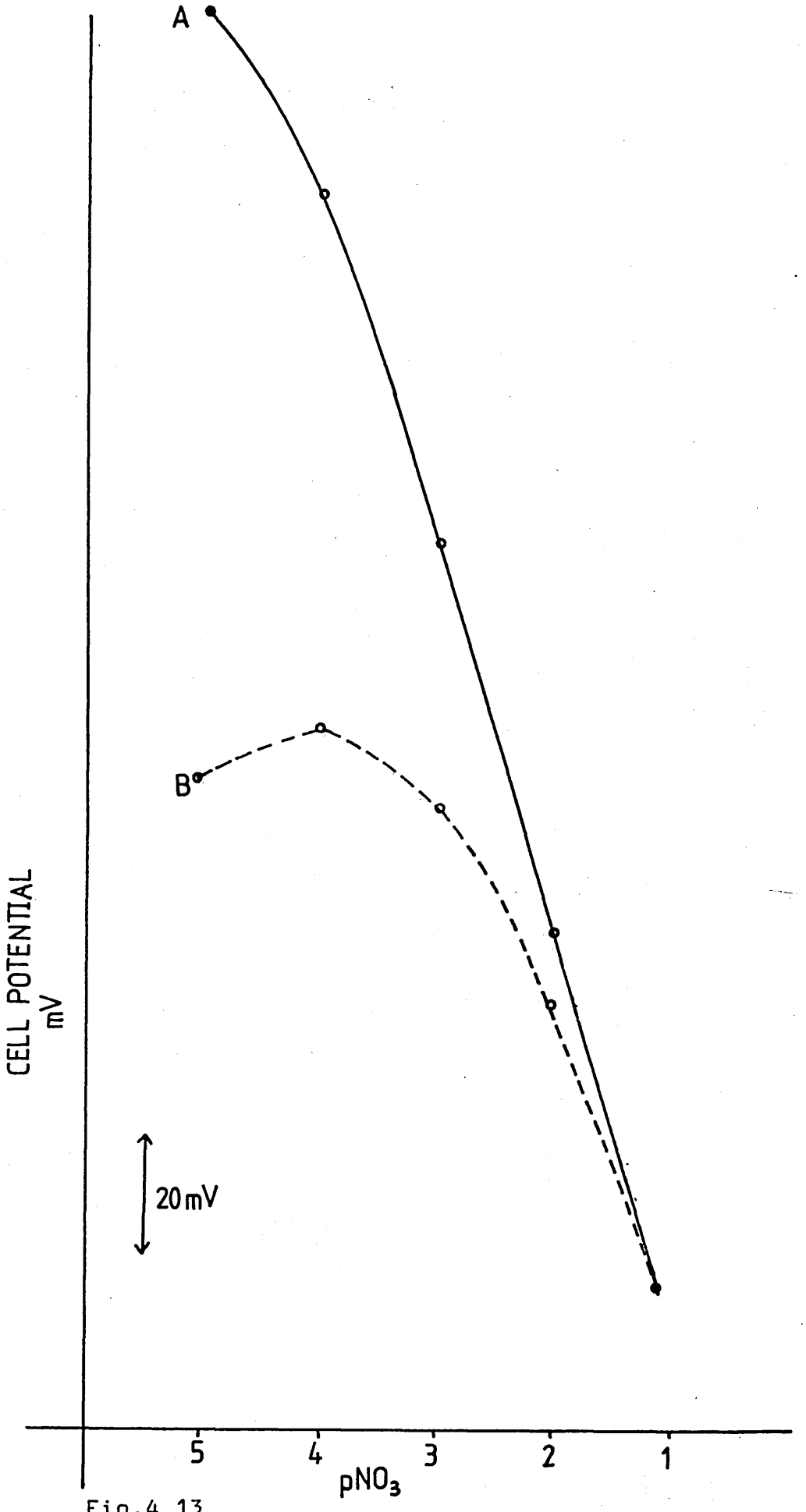


Fig.4.13
The response of master membrane JUNE 3 to unbuffered standards (A) and nitrate standards buffered with potassium dihydrogen orthophosphate (B).

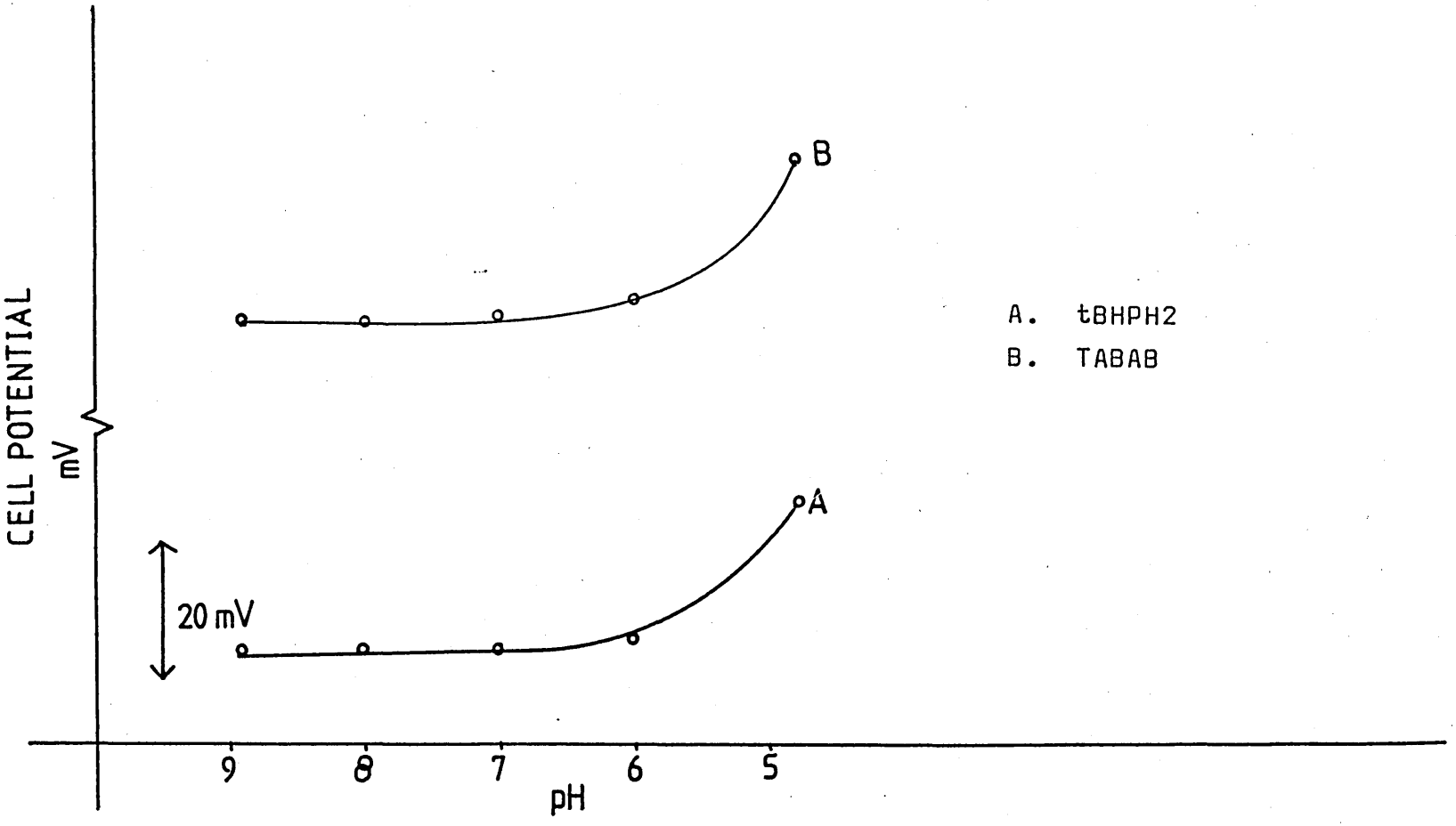


Fig.4.14
The response of membranes tBHPH2 and JUNE3 in 10^{-2} mol dm^{-3} KNO_3 solutions buffered with K_2HPO_4 and KH_2PO_4.

CHAPTER 5

THE USE OF MEDIATORS

5.1 Introduction

The membranes described in the previous chapter showed several useful properties including robustness, fast response, and long lifetimes. However, they were not sufficiently selective for nitrate, in the presence of other ions, for practical applications. Polymer membrane electrodes are usually prepared from three major components; a polymer, a sensor and a mediator or plasticiser. PVC membranes appear to always require one component of the membrane to act as a plasticiser. A plasticiser is a "softener" but also provides a medium for mobility within the membrane. Many PVC membranes were evolved from the equivalent liquid membrane; the liquid ion-exchanger was entangled with PVC to provide a polymer membrane[64]. The solvent present in the original liquid membrane often acted as a plasticiser for the PVC membrane. However the solvent was sometimes incompatible with PVC, or if compatible failed to plasticise the polymer. On these occasions standard plasticisers, from polymer technology, as opposed to electrode technology, were often added to the membranes to provide the plasticising function without necessarily contributing to the electroanalytical properties of the membrane. Solvent mediators usually influence the selectivity of the resulting membrane, and may also act as plasticisers.

Plasticisers although necessary for the normal functioning of the membrane may not have any influence on the electroanalytical properties of the membrane. The properties of solvent mediators necessary, as supporting medium of a liquid membrane can be clearly defined:

a) the solvent should be immiscible with water;

b) the viscosity of the medium should allow mobility of the ion-exchange sites;

c) the solvent should enhance the selectivity of the membrane;

d) the solvent should not adversely effect electrical properties such as resistance.

These requirements are still applicable to polymer membranes, although the viscosity of the medium is controlled by the polymer not the solvent mediator.

The triblock copolymer elastomer SBS, unlike PVC, does not require a plasticiser or mediator to function effectively as an electrode membrane. However, the selectivity of these SBS membranes may be improved by incorporating a mediator into the polymer. The pores of PVC membranes are reduced to macromolecular dimensions[113] by the combination of PVC and plasticiser;SBS polymer membranes probably have a more open network. The pore size of SBS membranes would be controlled by the extent of cross-linking introduced during the production of the membrane. The penetration of aqueous solutions into the

polymer network is therefore prevented only by the extent of cross-linking and the hydrophobic nature of the polymer. The uptake of water by SBS polymer was noted during conditioning when the polymers became white and opaque. The highly cross-linked polymers tBHPA-F (Table 4.4) showed less tendency to absorb water and did not become opaque. If aqueous solutions are able to diffuse through the polymer, the only control on selectivity is the sensor.. In the case of SBS membranes, with covalently bound quaternary nitrogen, poor selectivity would be expected under these circumstances, because quaternary ammonium salts are used as sensors for a number of ions including chloride. If the voids of the SBS network were filled with an uncharged mediator of suitable properties to encourage preferential exchange of nitrate ions at the membrane solution interface and prevent uptake of aqueous solutions, a more selective electrode could result.

5.2 Choice of Solvent Mediator

The influence of solvent mediators on selectivity is thought to be governed by the principles of solvent extraction. The extraction of one species from a solution can be achieved using a solvent immiscible with the solution, which offers a more stable environment. The stability of ions in solutions depends upon the dissipation of charge, and is related to the dielectric constant for a particular solvent.

TABLE 5.1

Solvent Mediators for Nitrate Electrodes

Solvent Mediator	Dielectric Constant	Sensor	Type of electrode	Ref.
dibutyl phthalate	dimethyl phthalate 8.5 ($24^{o}C$)	tetradodecylammonium nitrate	PVC	66
o-nitrophenyloctyl ether	23.5 [122] ($25^{o}C$)	tridodecylhexadecyl ammonium nitrate	PVC	65
decanol	8.1 ($20^{o}C$)	methyltrioctanoyl ammonium nitrate	Liquid	61,62
o-nitrophenyloctyl ether	23.5 ($25^{o}C$)	tris(bathophenanthroline) nickel(II) nitrate	PVC and liquid	114
ethyl bromide	methyl bromide 9.82 ($20^{o}C$)	tetra-amylphosphonium nitrate	Liquid	115

5.2.1 Dielectric Constant

When two ions are separated by a distance r, their potential energy of interaction is proportional to $1/(4\pi\varepsilon_o r)$ when the medium separating them is a vacuum (ε_o = permittivity of a vacuum). When the separating medium is a solvent their potential energy of interaction is reduced to $(1/(4\pi\varepsilon_o K_r r)$ where K_r is the relative permittivity or dielectric constant of the solvent. The dielectric constant is determined in part by the polar nature of the solvent molecules and it can have a significant effect on the strength of the coulombic interactions between ions. Water has a dielectric constant of 78, therefore the coulombic potential of ions dissolved in water are reduced by nearly two orders of magnitude compared to that in a vacuum.

5.2.2 Solvent Mediators used in Nitrate Electrodes

The first ion-selective liquid membranes were prepared from an ion-exchanger material, and a water immiscible solvent. The type of solvent used for liquid membranes was usually a non-polar organic liquid of low dielectric constant. Similar materials have been used as plasticisers for PVC membranes. The organic liquids listed in Table 5.1 have been used as solvent mediators for nitrate electrodes, the type of electrode and sensor for each mediator is also shown. To study the role of solvent mediators in SBS membranes, with covalently bound quaternary ammonium salts,

the following materials were chosen as 'mediators':

a) decanol (Aldrich)

b) dibutyl phthalate (Aldrich)

c) ethyl iodide(Aldrich)

d) methyl-p-toluenesulphonate (Aldrich)

e) O-nitrophenyloctyl ether (Fluka).

With the exception of methyl-p-toluenesulphonate these organic liquids have been used in ion-selective electrodes (ethyl bromide Table 5.1 was replaced by ethyl iodide for this work). The dielectric constant of decanol dimethyl phthalate, methyl bromide and o-nitrophenyloctyl ether are shown in Table 5.1.

5.2.3 Initial Investigations

The effects of solvent mediator on SBS membrane with covalently bound QAS were evaluated after impregnation of the membranes with mediators by soaking pieces of master membrane tBHPH Table 2.9, in the chosen mediator, or a solution of mediator and methanol. The membranes were allowed to absorb the mediator or solution for a number of hours, then washed with methanol, blotted dry and conditioned in 10^{-1} mol dm^{-3} $NaNO_3$. The master membrane tBHPH was used for all mediator studies because it was well characterised and showed reproducible electroanalytical properties. Three types of experiment were carried out with the mediators:

(i) A piece of membrane was placed in each of the mediators for a period of 2-8 hours.

(ii) A piece of membrane was placed in a 1:1 solution of mediator and methanol for a period of 2-8 hours.

(iii) A piece of membrane was placed in a 1:9 solution of mediator and methanol for a period of 2-8 hours.

The mediated membranes prepared by (i) were soft and easily damaged. The response of these membranes to nitrate solutions was evaluated using the Philips IS561 electrode body with the normal aperture, but several of the membranes ruptured during calibration. The softening and weakening of the polymer caused by the addition of mediator rendered these membranes unsuitable for practical applications.

The membranes resulting from experiments (ii) and (iii) were more robust, although even short exposure to the most dilute solution of mediator was detrimental to the mechanical properties of the polymer. The response of membranes treated with ethyl iodide (1:9), methyl-p-toluenesulphonate (1:1), and O-nitrophenyloctyl ether (1:1) in methanol are shown in Figures 5.1, 5.2 and 5.3 respectively. The response time of the membranes increased significantly compared to that of tBHPH (Figure 4.7) for all membranes, and was subject to drift.

The membranes treated with decanol were the least swollen and easiest to handle, but after conditioning, even these membranes showed poor response to nitrate solutions (16mV change in potential over 4 decades). The membranes

treated with dibutyl phthalate showed the greatest swelling, and were too soft for accurate calibration because they showed a tendency to leak or split.

The response of the membrane treated with ethyl iodide was encouraging because in this case an extended linear range was observed. However the presence of 10^{-2} mol dm^{-3} buffer solution interfered strongly below 10^{-2} mol dm^{-3}. The selectivity of the membrane for nitrate was not enhanced by the presence of ethyl iodide (Figure 5.1). A similar response was obtained from the membrane treated with methylp-toluenesulphonate, but the slope of the response was slightly lower and the membrane was less selective for nitrate in the presence of buffer (Figure 5.2). The membrane treated with O-nitrophenyloctyl ether showed a superior response to nitrate with linear response to 10^{-4} mol dm^{-3} and useful response to 10^{-6} mol dm^{-3} (Figure 5.3). This membrane also showed greater selectivity for nitrate in the presence of buffer solution. However, the membrane responded slowly and drifting potentials were experienced. The drift was such as to lower the linear working range.

The treatment of membranes with solvent mediators by these methods was less than satisfactory since the amount of mediator absorbed and retained by the membranes was difficult to quantify, and the physical affects of the mediator on the polymer structure rendered the membranes mechanically weak and easily damaged.

A. Unbuffered solutions.
B. Buffered solutions.
C. Untreated tBHPH buffered solutions.

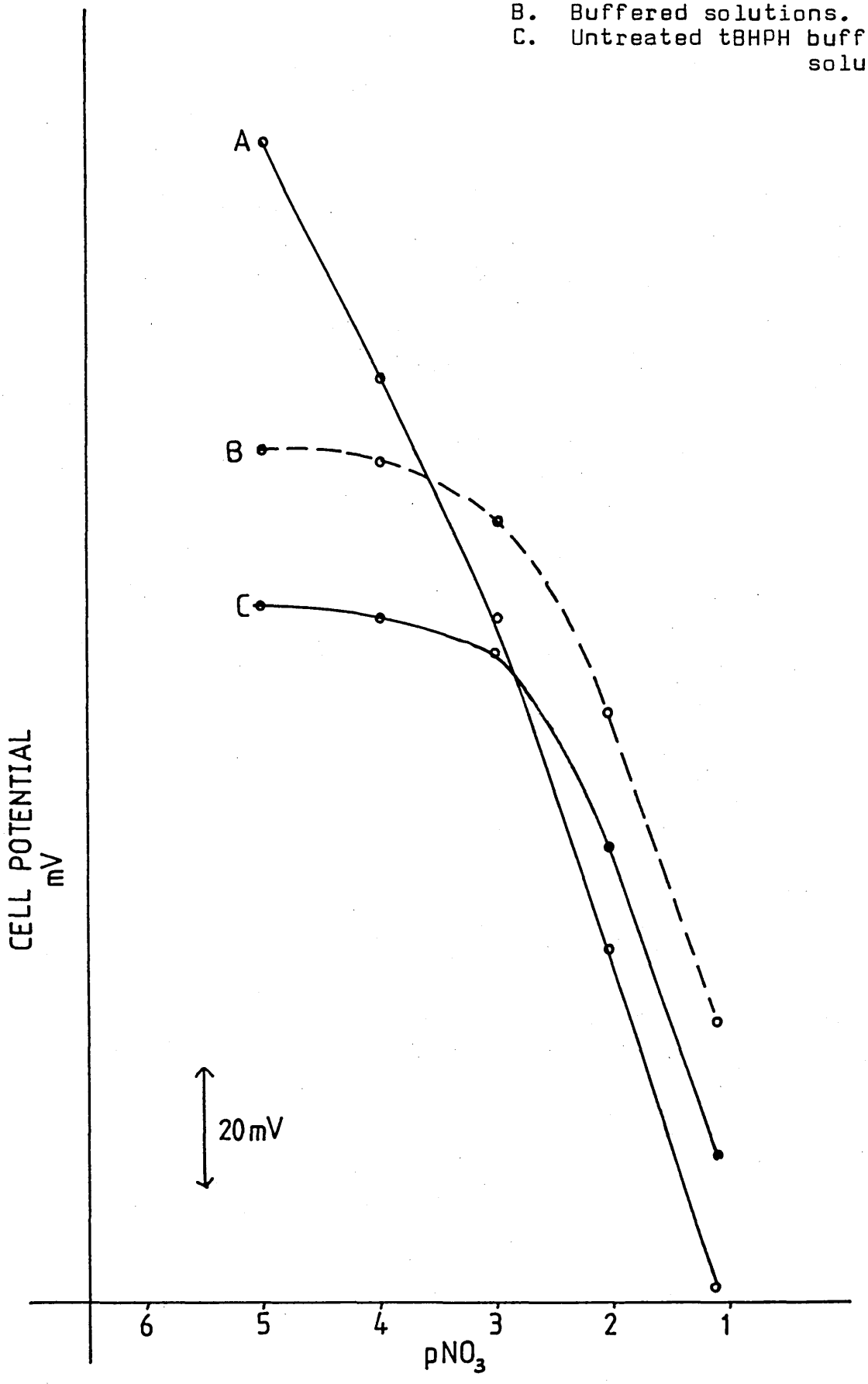


Fig.5.1
The response of tBHPH membranes impregnated with ethyl iodide ... compared with response of untreated tBHPH membrane (C).

A. Unbuffered solutions.
B. Buffered solutions.
C. Untreated tBHPH buffered solutions.

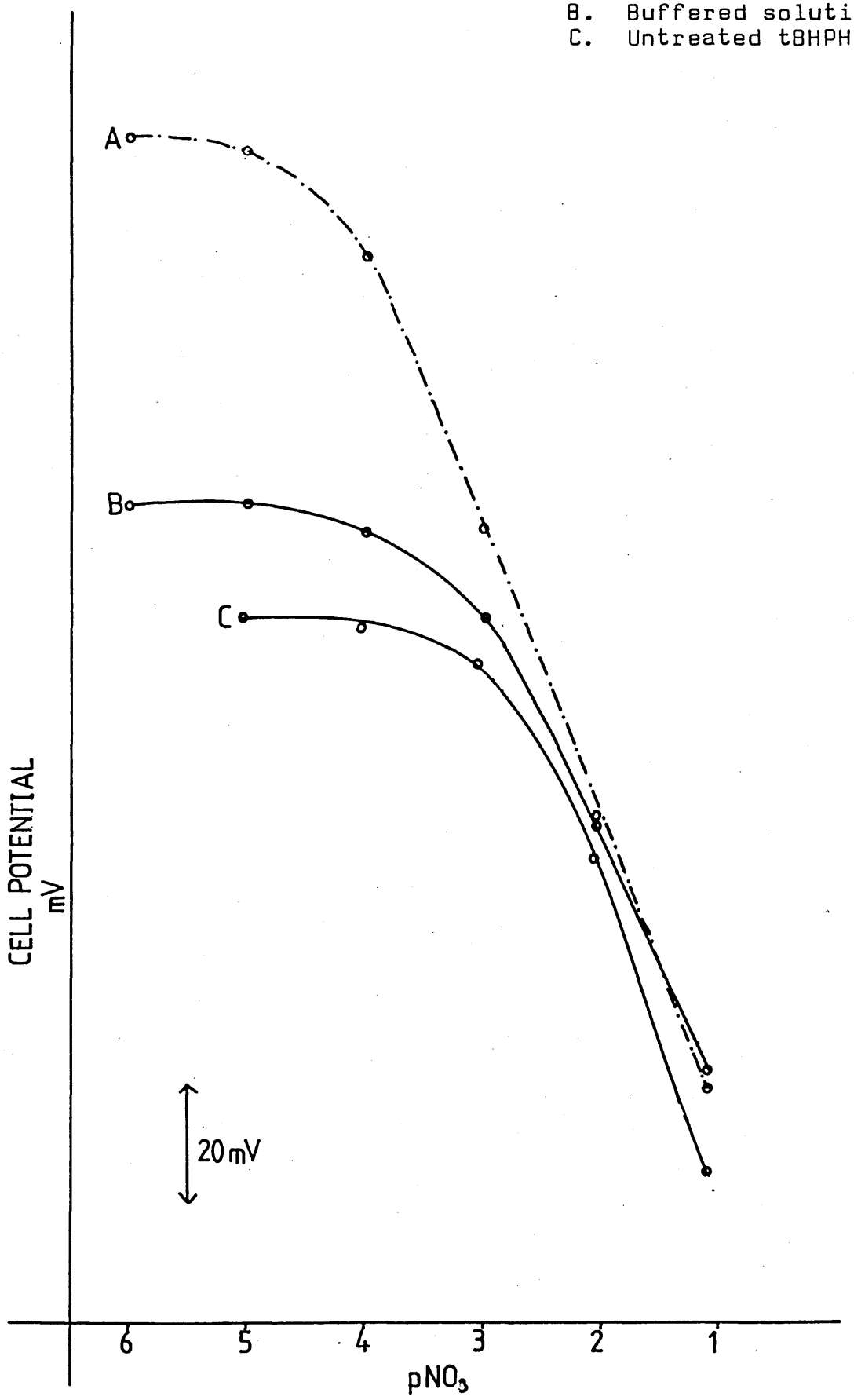


Fig.5.2
The response of tBHPH membranes impregnated with Methyl-p-toluenesulphonate compared with response of untreated tBHPH membrane (C).

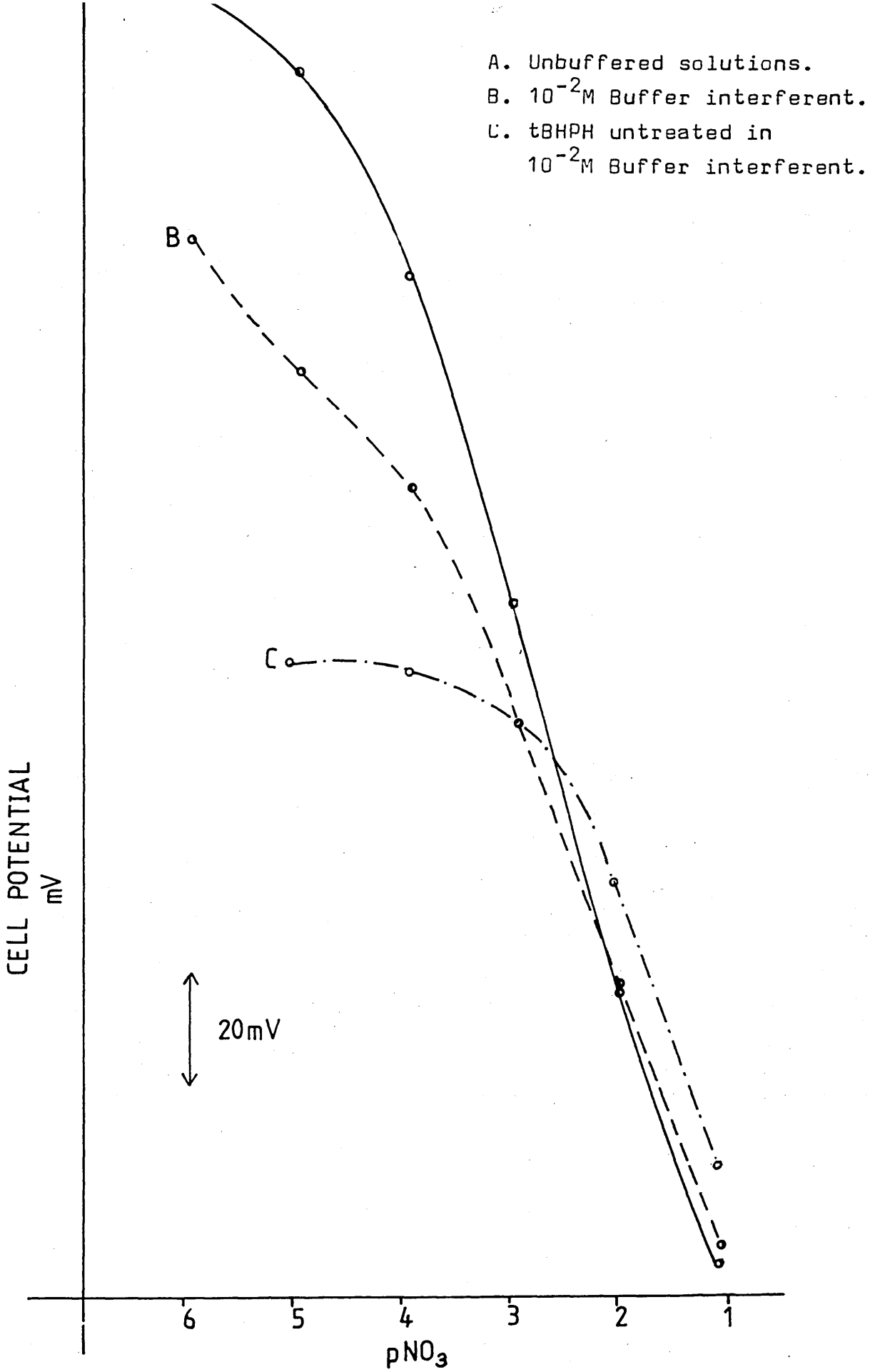


Fig.5.3
The response of tBHPH impregnated with O-nitrophenyloctyl ether.

TABLE 5.2

Membranes Prepared with Entangled Mediators

Master Membrane	SBS (g)	MEDIATOR Type	MEDIATOR Amount (g)	% W/W[a]	QAS (TAEAB)[b] (g)	tBHP[c] (g)	Comment
ENT 1	2.5	Ethyl Iodide	0.0733	2.93	0.2537	0.0458	Greasy, Yellow not cross-linke
ENT 2	2.5	Methyl p-toluene sulphonate	0.1297	5.19	0.2550	0.0450	Slightly Yellow Clear, Greasy not cross-linke
ENT 3	2.5	"	0.0743	2.97	0.2641	0.0391	Homogeneous, not transparent cross-linked
ENT 4	2.5	O-nitrophenyl octyl ether	0.0644	2.58	0.2530	0.0381	Yellow, transparent cross-linked

a Mediator/SBS% W/W

b TAEAB - Triallylethylammonium bromide

c tBHP

5.3 Solvent Casting with Mediators

The conventional method of membrane preparation is to combine all the membrane components before the process of solvent casting. This method of preparation was evaluated for SBS membranes using ethyl iodide, methyl p-toluenesulphonate and o-nitrophenyloctyl ether as mediators

The membranes listed in Table 5.2 were prepared using tBHP initiator by the method described in Section 2.3.2.3. A 35-70% W/W mediator/polymer mixture is often used for PVC membranes. However in this work mediators were found to inhibit cross-linking reactions in SBS membranes at much lower levels (Table 5.2). The membranes prepared with the different mediators were homogeneous with no inclusions or precipitation of polymer or mediator, although the texture of the polymer was generally very greasy. The membranes were conditioned, and the response to nitrate was evaluated using the modified Philips IS561 electrode body (see Section 3.2.1.4).

The cross-linked membranes showed Nernstian response from 10^{-1} to 10^{-3} mol dm^{-3} but poor response in dilute solutions. All the membranes showed rapid deterioration in response during use similar to that observed previously for membranes prepared with high levels of QAS. The presence of the mediator may inhibit the reactions leading to covalent attachment of the QAS to the polymer backbone,

although some cross-linking was observed. The membranes prepared with ethyl iodide and O-nitrophenyloctyl ether showed the most rapid deterioration in response. The O-nitrophenyloctyl ether membrane showed deterioration from Nernstian response over 2 decades to a response of 10mV over 4 decades of nitrate activity. The rate of deterioration was slower for the membrane prepared with methyl-p-toluenesulphonate. The rate of deterioration could be related to the extent of inhibition of the cross-linking reaction, or the increase in hydrophobicity of the polymer by the inclusion of mediator which causes a reduction in leaching.

5.4 Selection and Preparation of a Mediator for Covalent Attachment

Including a conventional mediator by entanglement in any polymer membrane limits the lifetime of the membrane because the mediator eventually leaches from the polymer thus causing a deterioration in the properties of the membrane. It is possible that no increase in lifetime would be achieved with covalently bound sensors, if the mediator was only entangled within the polymer. The detrimental effect of introducing conventional mediators into SBS polymer preparations was demonstrated by the previous examples.

In an attempt to extend the lifetime of the membranes and improve their selectivity a new type of mediator was

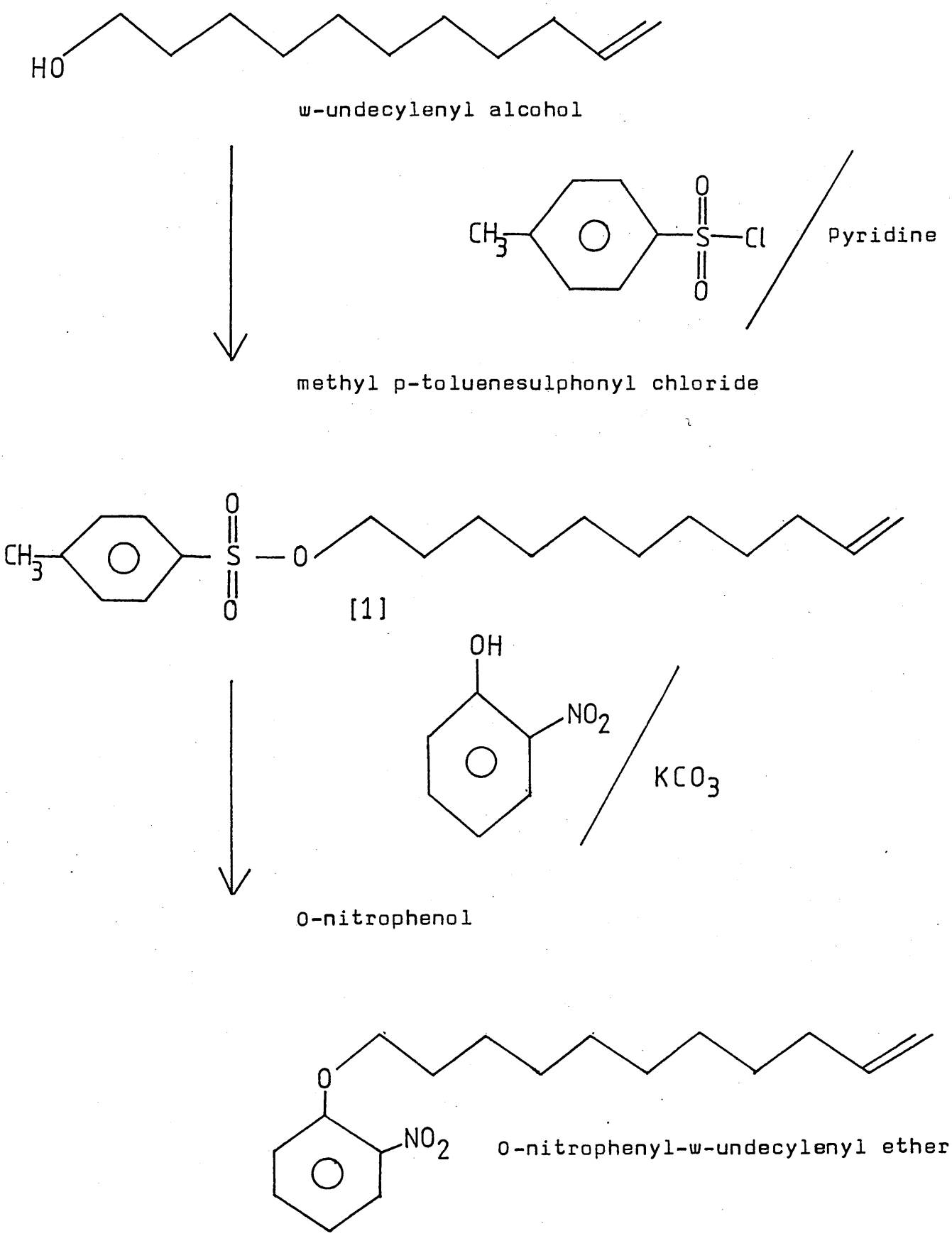


Fig. 5.4 Synthesis of o-nitrophenyl-w-undecylenyl ether.

prepared. The mediator (Figure 5.4) was based on the o-nitrophenyloctyl ether structure which is used commercially as a mediator for nitrate electrodes and enhanced the selectivity of SBS membranes. The double bond was introduced to enable the mediator to participate in cross-linking reactions to produce a membrane with covalently bound sensor and mediator.

5.4.1 Experimental

5.4.1.1 Preparation of ω-Undecylenyl p-toluenesulphonate [116]

ω-Undecylenyl alcohol (25g), p-toluenesulphonyl chloride (25g) and pyridine (38g) were stirred in a 500cm^3 round-bottom flask at room temperature for 24 hours. The mixture was then treated with dilute hydrochloric acid to neutralise the pyridine and the tosylate separated from the acid solution as a heavy oil and was collected by extraction with diethyl ether (2x25cm^3). The extracts were dried over magnesium sulphate, filtered, the ether removed under vacuum and the tosylate (28g) obtained as a semi-solid which was not recrystallised. Infra-red spectroscopy and thin layer chromatography indicated the presence of a small amount of alcohol in the product.

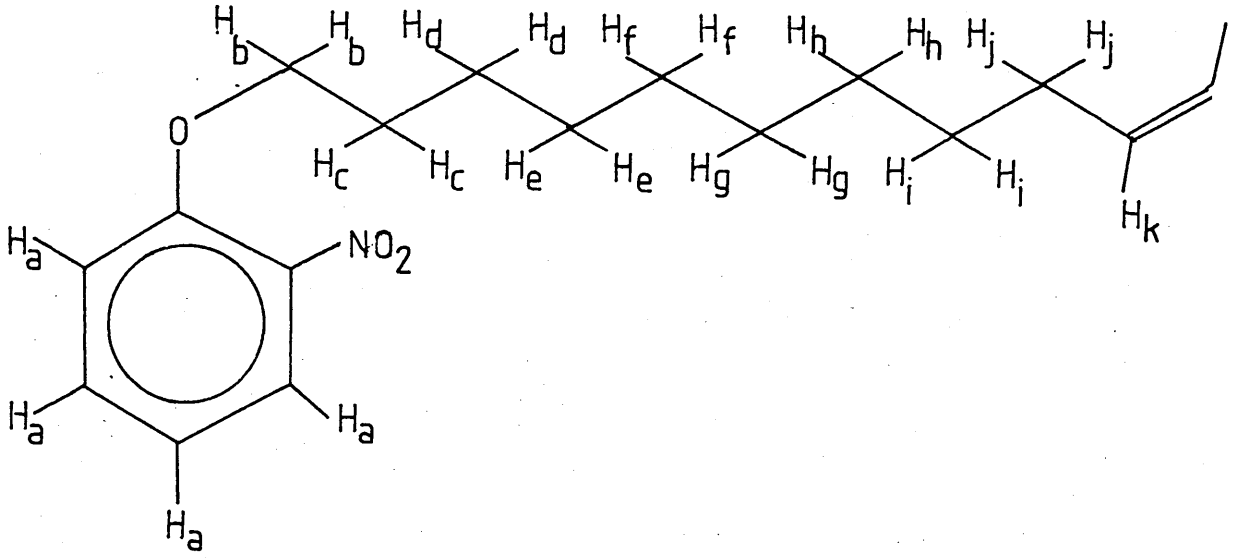
5.4.1.2 Preparation of o-nitrophenyl-ω-undecylenyl ether

ω- Undecylenyl p-toluenesulphonate (14.5g) was refluxed for 24 hours with o-nitrophenol (6.5g) and anhydrous potassium carbonate (5.6g) in dry acetone (100cm^3).[117]

TABLE 5.3

'Hnmr Characterisation of
O-nitrophenyl-ω-Undecylenyl ether

δ/ppm[a]	H atom	relative intensity
7.0 - 7.85m.	H_a	3.5
5.0t. 5.5 - 6.3m	H_k - H_l	3.6
4.15q	H_b	3.5
1.5 - 2.5	H_c - H_j	3.9



a. Solvent. $CDCl_3$

The flask was shaken occasionally to prevent accumulation of solid material, and the reaction followed by thin layer of chromatography. The mixture was cooled, diluted with water ($100cm^3$) and extracted with benzene ($2x50cm^3$). The extracts were washed with sodium hydroxide solution ($2x50cm^3$) and dried over magnesium sulphate. The benzene was removed by distillation at normal pressure and the product distilled under reduced pressure to yield a yellow-green oil (5.91g) at $166^oC/0.03mmHg$, using a bunsen flame and an air condenser.

The product was characterised by nmr(Table 5.3) and infrared spectroscopy and shown to be pure using thin layer chromatography.

5.4.2 Evaluation of O-Nitrophenyl-*ω*-undecylenyl ether as a Mediator.

The conventional mediating properties of this new material were assessed by Kent Industrial Measurements Ltd. The mediator was used as the supporting solvent in an E.I.L. liquid membrane electrode. The resulting electrode showed Nernstian response to nitrate, of 61mV per decade at 30^oC, with linear response to $2x10^{-5}$ mol dm^{-3} in the presence of 10^{-1} mol dm^{-3} potassium dihydrogen phosphate buffer. This response was slightly inferior to the normal E.I.L. liquid membrane. However the selectivity of the new mediator for nitrate assessed by the mixed solution method using 10^{-2}mol dm^{-3} potassium chloride was $7x10^{-3}$ which was superior to the E.I.L. liquid membrane but inferior to the E.I.L. PVC membrane electrode. The

TABLE 5.4

Membranes Prepared with Mediators

Master Membrane	SBS (g)	QAS Type	QAS Amount	% W/W[b]	tBHP (g)	Mediator (g)	% W/W[e]	Comments
MED 1	2.50	-	-	-	0.1106	0.3785[c]	15.14	Smooth, Clear, Firm, cross-linked. ($0.5cm^3$ Methanol)
MED 2	2.50	TAEAB[a]	0.2470	9.88	0.1327	0.2767	11.07	Yellow, contains cl liquid pools within membrane, possibly result of the media separating from the polymer. The edges of the po are cross-linked. ($2.0cm^3$ Methanol)
MED 3	2.50	TAEAB[a]	0.2492	9.97	0.1813	0.2979[c]	11.92	Clear, Slightly yel cross-linked. (1.0cm metha
MED 4	2.50	TAEAB[a]	0.2540	10.16	0.1365 0.1510	0.3042[c]	12.17	Two Stage Cross-lin method, ($2.0cm^3$ Methanol)
MED 5	2.50	TAEAB[a]	0.2564	10.26	0.1074 0.1010	0.3083[d]	12.33	Two Stage Cross-lin methanol. ($2.0cm^3$ Methan

a TAEAB Triallylethylammonium bromide
b % W/W QAS/SBS
c O-nitrophenyl-ω-undecylenyl ether
d ω-Undecylenyl p-toluenesulphonate
e % W/W Mediator/SBS

electrode showed fast response times. The mediating properties of this new material were thus confirmed by this performance as a solvent mediator in a conventional liquid membrane electrode.

5.4.3 Preparation of Membranes with a Covalently Bound Mediator

A membrane was prepared with 50% W/W polymer/mediator, with normal levels of tBHP initiator and without QAS. The resulting membrane was transparent, yellow, flaccid and gelatinous and no cross-linking was observed. A further series of membranes was prepared with lower levels of mediator as shown in Table 5.4, in an attempt to optimise the composition of the membrane and obtain covalent attachment of QAS and mediator. The membrane MED2 was not homogeneous and pools of liquid were clearly visible within the polymer. The appearance of this membrane suggested that some separation of membrane components during solvent-casting. This separation was not observed with MED1 which did not contain QAS. The amount of methanol in the polymers was reduced to a minimum to prevent separation of the membrane components. Methanol was used to bring the QAS into solution. The master membrane MED3 was homogeneous and cross-linked. The new membranes MED2 and MED3 were conditioned and their response to nitrate evaluated using the Philips IS561 electrode body. The response of the membranes, shown in Figure 5.5, was poor and did not improve with further conditioning. The master membrane MED2 showed varying response to nitrate with long response times and drifting

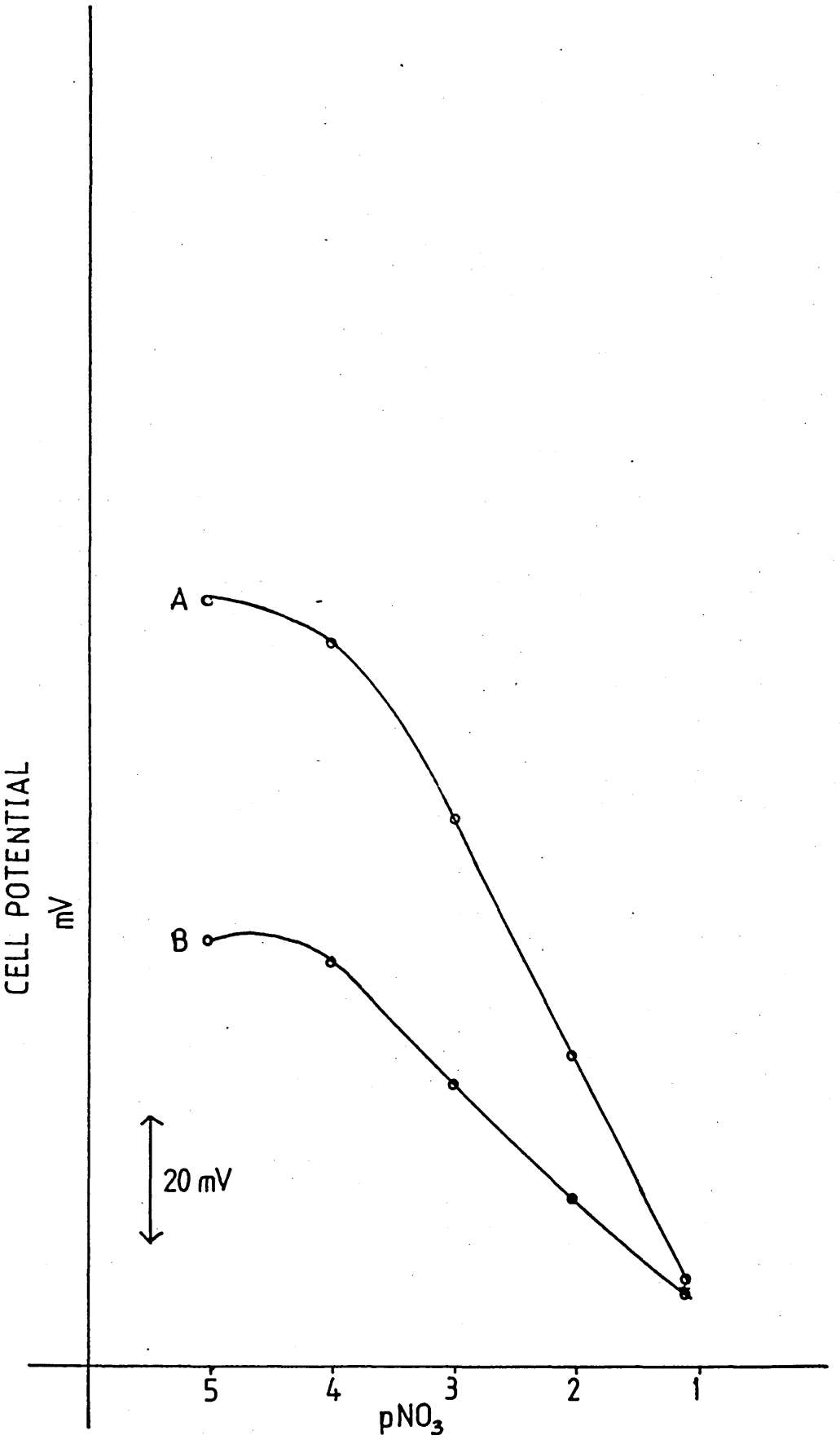


Fig.5.5
The response of Master Membranes MED2(A) and MED3(B)to nitrate solutions.

TABLE 5.5

Properties of Solvent Cast Mediated Membranes

Master Membrane	% Nitrogen (Kjeldahl Analysis)[a]	% Nitrogen (Expected) QAS	Mediator	Total	Cross-linked Density Moles Cross-links cm^{-3}	Resistance/Ohms) Unconditioned	Condit
MED 1	I[b] 0.31 E 0.39	-	0.63	0.63	Not cross-linked	-	-
MED 2	C 0.13 E 0.31	0.47	0.44	0.91	$4.57\ 10^{-6}$ (Edge Pieces)	8.5×10^{9}	3×1
MED 3	C 0.02 I 0.05 E 0.41	0.47	0.47	0.94	4.5710^{-6}	2.0×10^{9}	10^{12}
MED 4	C 0.56 I 0.40 E 0.62	0.47	0.48	0.95	1.39×10^{-5}	5×10^{11}	$1.6 \times$
MED 5	C 0.22 I 0.29 E 0.40	0.48	-	0.48	9.3×10^{-5}	8.5×10^{12}	6×1

a. 24 hour Extraction before analysis

b. C - Central area of membrane
I - Intermediate area of membrane
E - Edge of membrane

potentials. However after extensive conditioning a stable response and fast response times were obtained for the calibration shown in Figure 5.5. The long response times and drifting potentials were attributed to the pools of mediator, which were removed by conditioning over an extended period.

The covalent attachment of nitrogen to the polymers MED1, MED2 and MED3 and the cross-linked density of the membranes is shown in Table 5.5. The membranes had similar cross-linked densities to membranes which did not contain a mediator (Table 4.5), but the amount of nitrogen present was low. The presence of the mediator appears to reduce the amount of QAS, which becomes bound to the polymer.

5.4.3.1 Two-Stage Solvent Casting

A new method of membrane preparation was used to overcome the compatability problems experienced with these membrane components, and to promote extensive cross-linking of both QAS and mediator to the polymer. The basic solvent-casting method was separated into two stages. First a solution of polymer, QAS and initiator was cast as described in Section 2.3.2.3. The membrane was semi-solid after 5-8 hours in an oven and then a solution of mediator and further initiator in THF was poured over the casting which was then replaced in the oven for a further 8-12 hours. The THF solution was expected to permeate the semi-solid polymer dispersing mediator throughout the polymer. The two competing or incompatible reactions were therefore separated and

homogeneous cross-linked membranes were obtained. This method was used to prepare membranes MED4 (Table 5.4) using the new mediator material, and also membrane MED5 using ω-Undecylenyl p-toluenesulphonate.The properties of these membranes were evaluated and are shown in Table 5.5. The cross-linked density of MED4 and MED5 was higher than MED2 and MED3 and MED4 contained more covalently bound nitrogen.

The membranes MED4 and MED5 were conditioned and their response to nitrate solutions was assessed using the modified Philips electrode body. The membrane MED4 showed distinct two-sided behaviour (Figure 5.6). The two sides of the membrane were different in appearance. The lower surface, which was in contact with the cellophane during membrane preparation, was smooth, and shiny. The upper surface, onto which the solution of mediator was poured during membrane preparation, was dull. The shiny side of the membrane showed similar response to the tBHP type membranes. The response was Nernstian from 10^{-1} to 10^{-4} mol dm^{-3} and extended response to 10^{-5} mol dm^{-3} was observed with a slope of 20-25mV (Figure 5.6(A)). The dull side of the membrane showed very poor response to nitrate, (Figure 5.6(B)) and a realistic reading for 10^{-5} mol dm^{-3} solution could not be obtained.

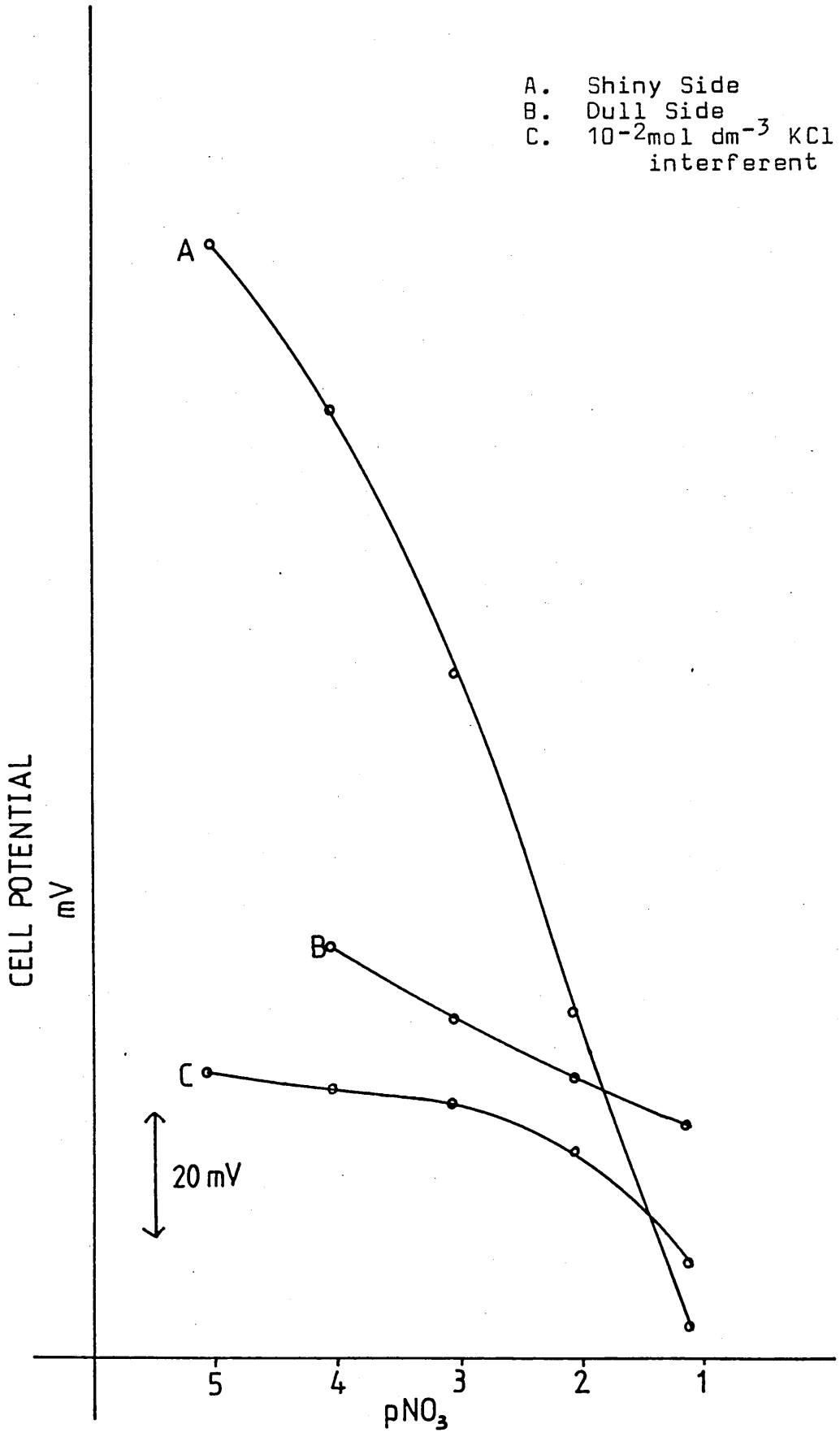


Fig.5.6
The response of master membrane MED4 (Unbuffered solutions)

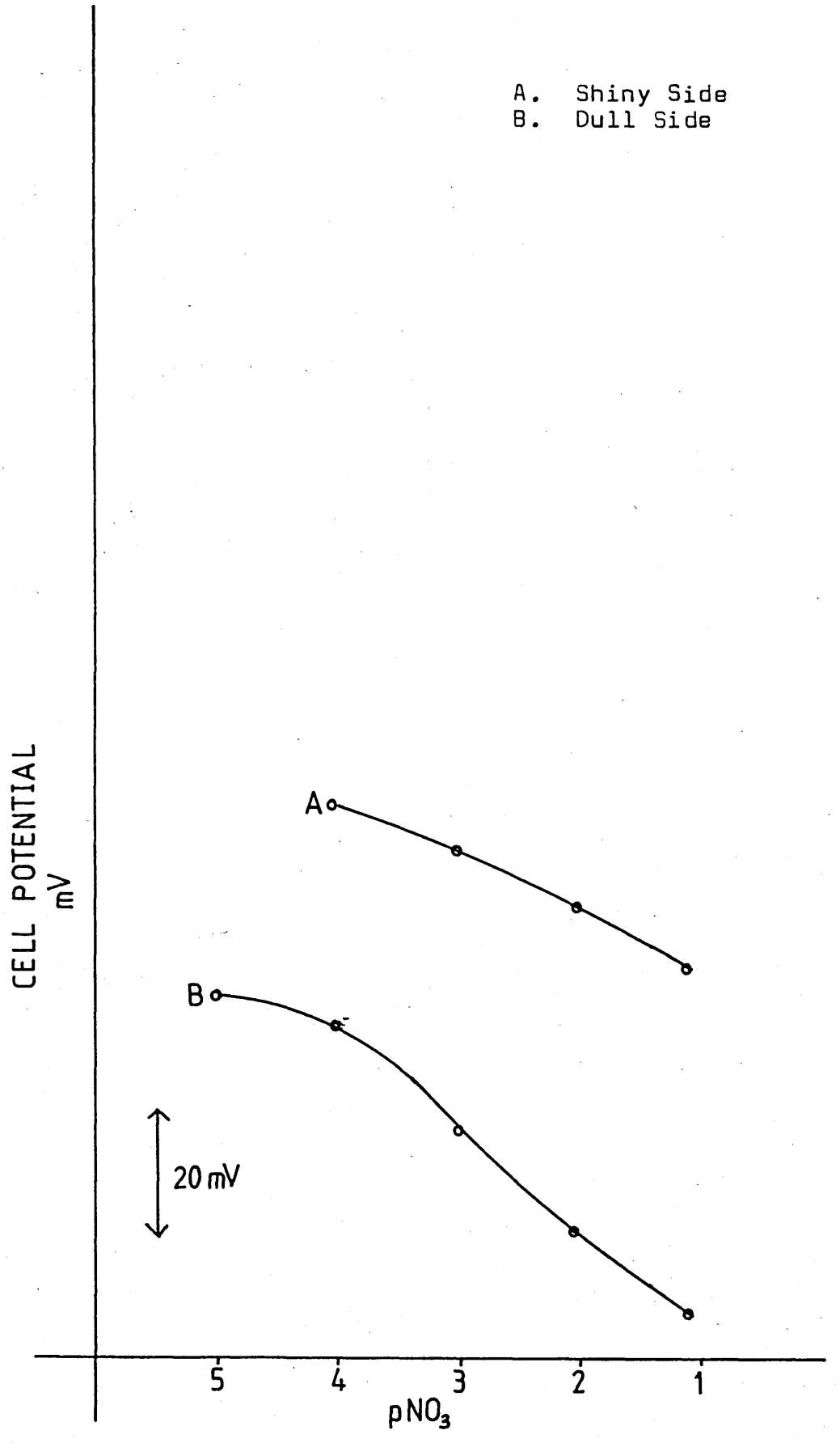


Fig.5.7
The response of master membrane MED5 (unbuffered soluti

The addition of a mediator to the membranes did not improve their sensitivity to nitrate ion. The shiny side of MED4 showed inferior response to nitrate when compared with some unmediated membranes; MAY10 showed similar extended response (Figure 4.10) and the master membrane JUNE3 showed superior range and slope (Figure 4.13). However the purpose of including the mediator was to improve the selectivity. Several of the earlier tBHP membranes showed acceptable response to nitrate and long lifetimes, but the application of the membranes in real situations was restricted by their very poor selectivity. Therefore although the response of MED4 was not an improvement, when compared to unmediated membranes, this response coupled with improved selectivity would broaden the possible applications of the membranes. The response of MED4 to nitrate solutions with 10^{-2} mol dm^{-3} chloride interferent is shown in Figure 5.6(C). The selectivity of the membrane was inferior to the selectivity of unmediated tBHPH membranes (Figure 4.6).

The membrane MED5 prepared with tosylate intermediate (1) (Figure 5.4) showed poor response to unbuffered nitrate solutions; the response of both sides of the membrane was similar (Figure 5.7). The response time behaviour of MED4 and MED5 was identical to that of unmediated membranes of tBHPH type (Figure 4.7).

The distinct, two-sided behaviour of membrane MED4 suggested that the two-stage method of membrane preparation had not produced a homogeneous membrane. The mediator may have dispersed throughout the membrane, but a layer of mediator was obviously concentrated on the upper (dull) side. The poor response of this side to nitrate solutions may be caused by the ion-exchange sites being covered by a layer of covalently bound mediator, preventing either conditioning or ion-exchange during response. Kjeldahl analysis of MED4 suggested that covalent attachment of both mediator and QAS had occurred. The average amount of covalently bound nitrogen was found to be 0.52% which is slightly higher than expected for either mediator or QAS alone. The extent of covalent attachment of QAS in the presence of O-nitrophenyl-ω-undecylenyl ether for membranes MED2 and MED3 also suggested that some of the covalently bound nitrogen resulted from mediator. Another helpful comparison was MED5 which was prepared by an identical method again with an unsaturated mediator, but covalent attachment of nitrogen was only from the QAS in this membrane (the mediator did not contain nitrogen).

5.5 The Response of Membranes Prepared with tBHP Initiator to Chloride and Sulphate.

The sensors chosen for this work, QAS, have been used by other workers[61,62] to prepare ion-selective membranes for a number of ions including chloride, nitrite and perchlorate. The membranes prepared in this work from QAS

and SBS have shown Nernstian response to nitrate but very poor selectivity. The response of membranes with covalently bound QAS to chloride and sulphate ions was assessed to determine their usefulness as selective membranes for other anions.

5.5.1 The Response of Membranes to Chloride

The master membranes MAY10, JUNE2, JUNE3, JUNE7, JUNE8, MED1, MED2, MED3, MED4, MED5 and the Philips PVC membrane from the IS561 nitrate electrode were selected, and a piece of each membrane was conditioned in 10^{-1}mol dm^{-3} NaCl for a minimum of 24 hours. The Philips IS561 electrode body was used for membrane calibration, but the internal filling solution was replaced by 10^{-1} mol dm^{-3} NaCl solution. Standard solutions were prepared with KCl (AnalaR) and the response of the membranes to chloride was evaluated as described in Section 3.2.2.4, but for chloride rather than nitrate response.

The Philips PVC membrane showed Nernstian response to chloride ions in the range 10^{-1} to 10^{-3} mol dm^{-3}, but poorer response in more dilute solutions The master membranes JUNE2 and JUNE3 were prepared from TAAB and TABAB respectively (Table 4.6). The membranes showed Nernstian response to nitrate in the range 10^{-1}-10^{-4} mol dm^{-3} (Figure 4.12). The response of JUNE2 and JUNE3 to chloride ions was poor but approximately linear to 10^{-5} mol dm^{-3} with a slope of 10mV per decade. The master membrane JUNE7 (Table 4.6) was

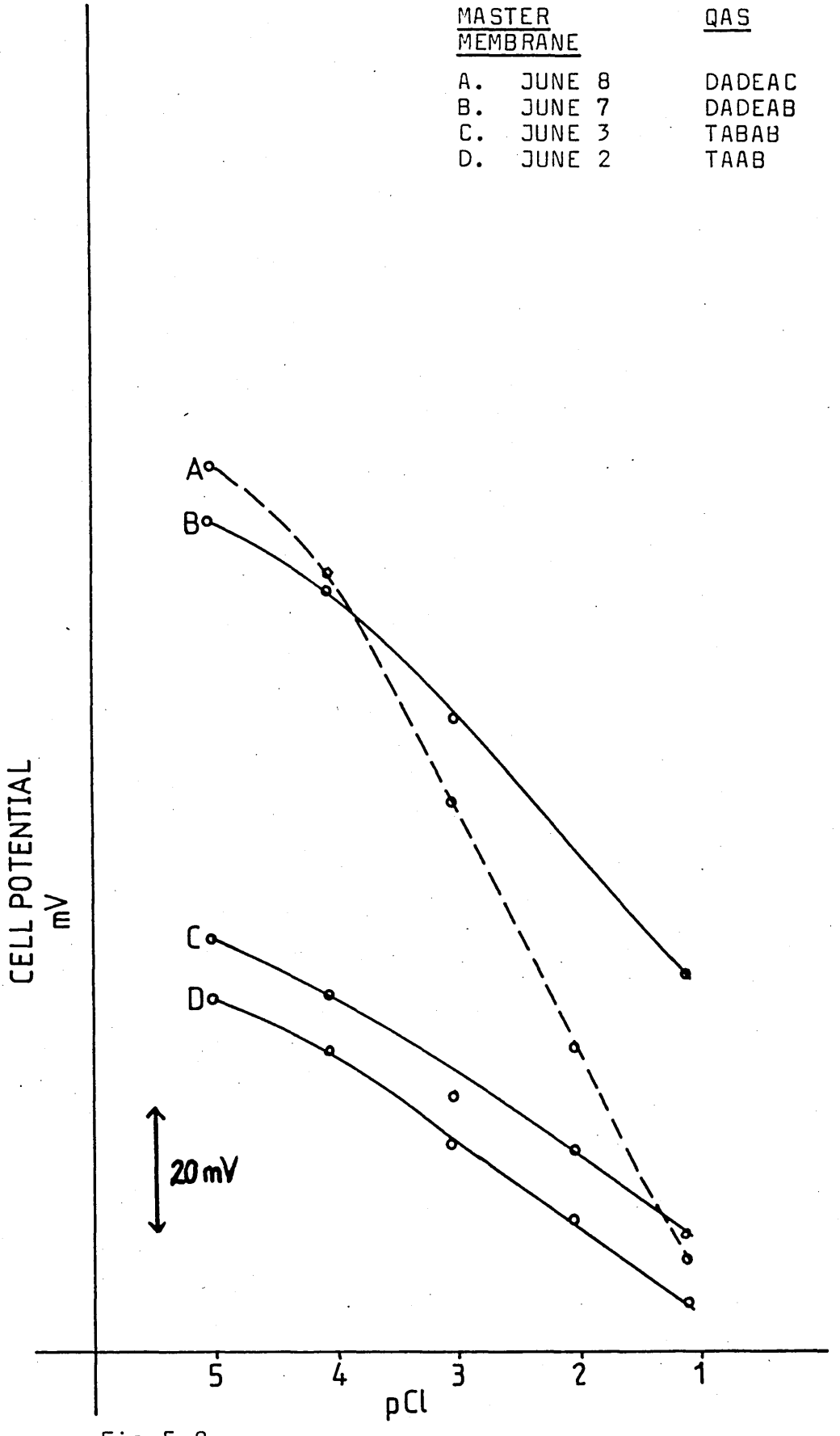


Fig.5.8
The response of membranes with different QAS to chloride standard solutions after conditioning with chloride solution.

prepared with DADEAB and showed similar response to chloride and nitrate ions (Figure 5.8 and Figure 4.11), with slopes of 20-25mV per decade for both ions. The master membrane JUNE8 was prepared with DADEAC and showed superior response to chloride ions, Figure 5.8, when compared to nitrate ions, Figure 4.11, particularly below 10^{-3} mol dm^{-3}.

The superior response of the membrane prepared with DADEAC to chloride ions may be a result of the chloride ion already being present in the polymer structure. The local structure of the polymer may be effected by the size of the counter-ion on the QAS. A large counter-ion may inhibit polymerisation or multiple covalent attachment; quaternary ammonium chlorides polymerise more readily than the equivalent bromides.[95] The polymer structure may be controlled by the counter-ion in a way which influences the cavity available for the ion within the polymer. A polymer prepared with a chloride counter-ion would thus be more sensitive to chloride than nitrate, chloride is the smaller ion of the two, so if cavity size was restricted chloride would be preferred.

The membranes prepared with entangled mediator showed superior response to chloride solutions Figure 5.9. The master membrane MED1, prepared with mediator and SBS but without QAS, showed some response to chloride after conditioning. It is possible that the covalently bound mediating molecule O-nitrophenyl-ω-undecylenyl ether lends

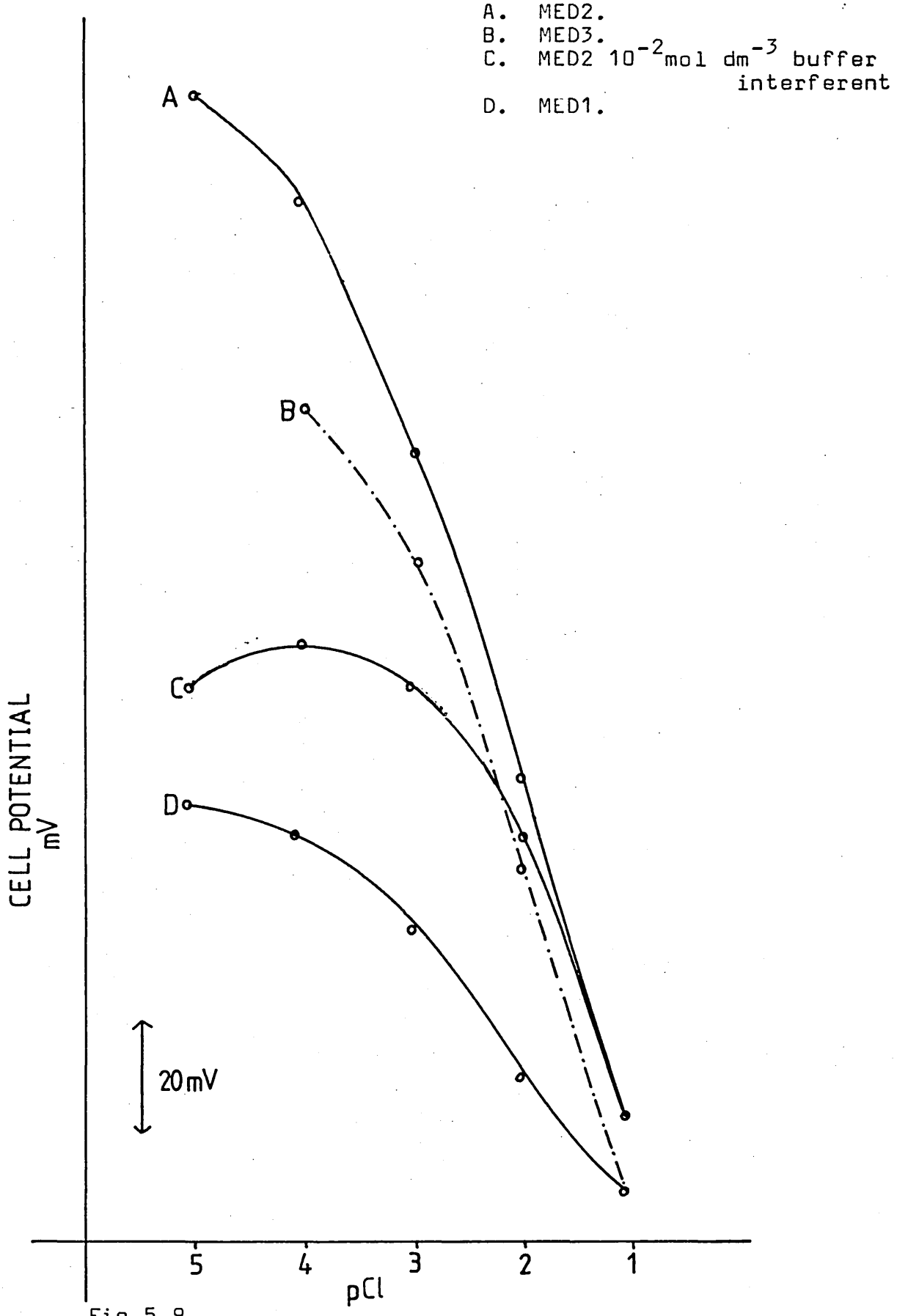


Fig.5.9
The response of master membranes MED1, MED2 and MED3 to chloride standard solutions.

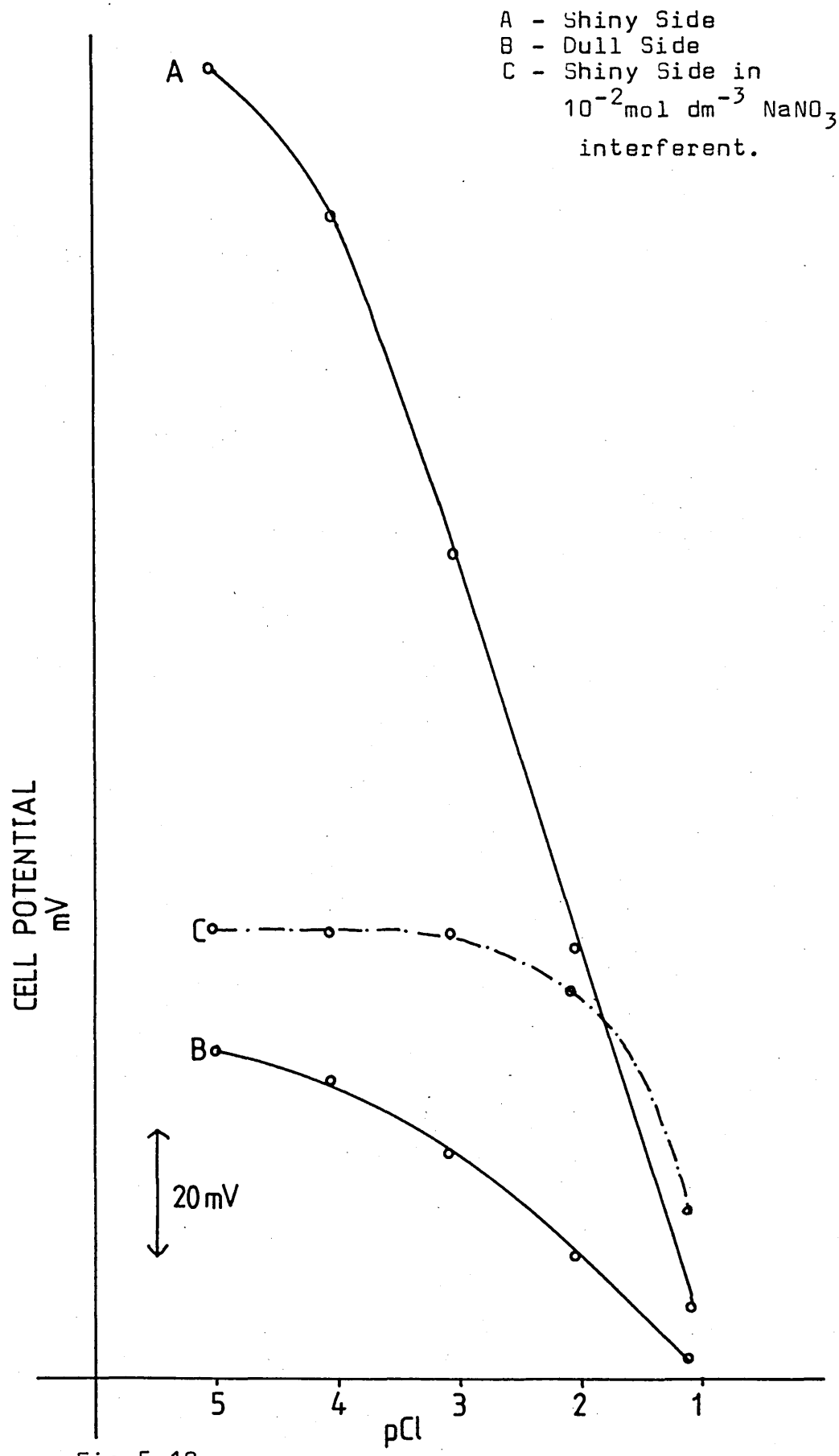


Fig.5.10
The response of master membrane MED4 to chloride stand solutions after conditioning in NaCl solution.

some chloride senstivity to SBS without providing ion-exchange sites. The membranes MED2 and MED3 also showed enhanced response to chloride ions although a realistic response for 10^{-5} mol dm^{-3} could not be obtained for MED3. The membranes were found to have poor selectivity for chloride ions. When MED2 was examined for selectivity, with 10^{-2} mol dm^{-3} buffer solution, the extent of interference was similar to that found for nitrate response.

The membrane MED4 showed two-sided behaviour when used as a chloride electrode membrane, similar to that experienced for nitrate. The shiny side of the membrane showed Nernstian response to chloride solutions from 10^{-1} to 10^{-4} mol dm^{-3} and useful response to 10^{-5} mol dm^{-3}. The mediator obviously lends some property to the membrane which improves sensitivity to chloride ions. The response to chloride ions of membranes prepared with mediator, by either one or two-stage preparation, is superior to the response of unmediated membranes. The excellent response of the shiny side of MED4 demonstrates that mediator is present throughout the membrane. If the mediator solution had not permeated the membrane the response of the shiny, unmediated side would be similar to the response of JUNE2 and JUNE3 (Figure 5.8). However, the purpose of including the mediating material was to improve the selectivity of the membranes to nitrate. The response of MED4 to chloride ions was strongly interfered with by 10^{-2} mol dm^{-3} $NaNO_3$

solution (Figure 5.10). The dull side of the membrane showed poor response to nitrate and chloride ions. The master membrane MED5, showed poor response to nitrate solutions, Figure 5.11 but linear response to chloride solutions with slope of approximately 40mV 10^{-1} to 10^{-4} mol dm^{-3}. The response to chloride was strongly interfered with by the presence of 10^{-2} mol dm^{-3} $NaNO_3$. The dull mediated side of the membrane showed poor response. Thus it seems doubtful if the compounds are worthy of further pursuit. Such evidence as there is suggests that they enhance rather than suppress response to chloride ions.

5.5.2 The Response of Membranes to Sulphate.

The master membranes MAY10 and JUNE2 were conditioned in 10^{-1} mol dm^{-3} Na_2SO_4 for a minimum of 24 hours. The response of the membranes to standard solutions of K_2SO_4 was evaluated using the Philips IS561 electrode body and the method outlined in Section 3.2.2.4. The master membrane JUNE2 showed Nernstian response 10^{-1} to 10^{-5}mol dm^{-3} but the response of MAY10 showed some deterioration below 10^{-4} mol dm^{-3}. The response of MAY10 to sulphate ions in the presence of 10^{-2} mol dm^{-3} KCl was very poor, the extent of interference is shown in Figure 5.12.

5.5.3 Conclusion

Polymer membranes prepared with covalently bound quaternary ammonium salts showed acceptable response to nitrate or sulphate ions after appropriate conditioning,

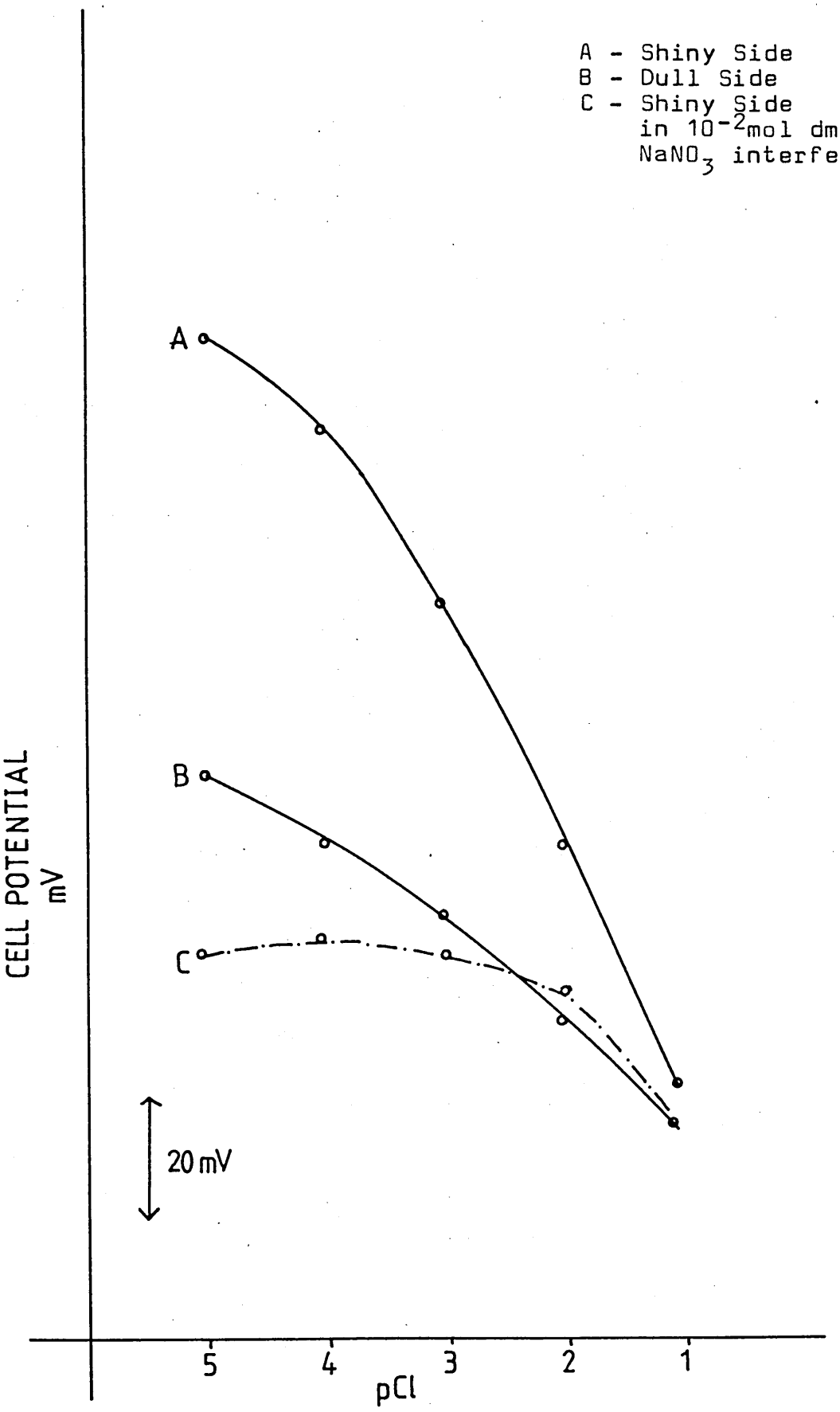


Fig.5.11
The response of master membrane MED5 to chloride standard solutions after conditioning in NaCl solution.

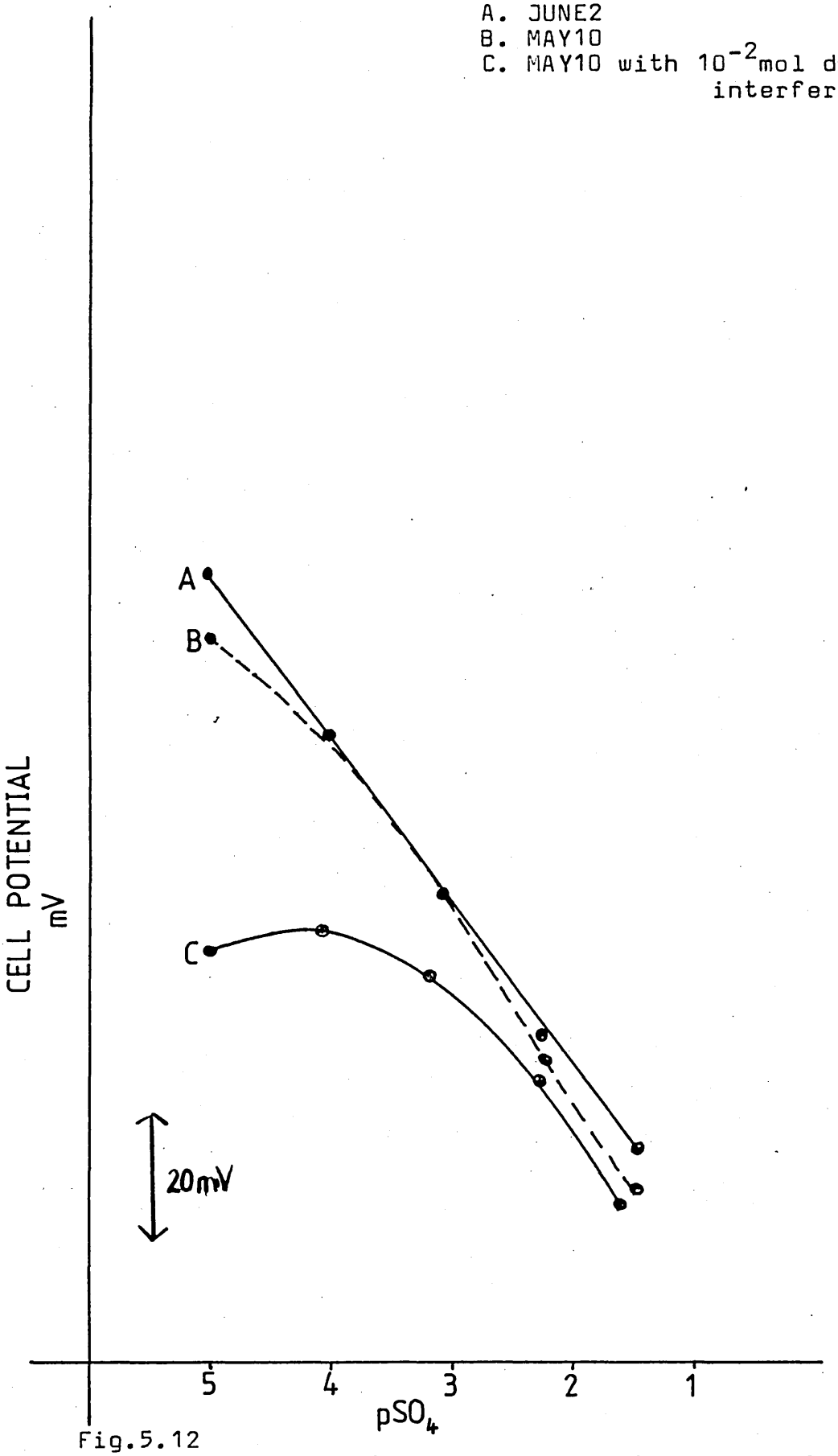


Fig.5.12
The response of master membranes MAY10 and JUNE2 to sulphate standard solutions after conditioning in 10^{-1}mol dm^{-3} Na_2SO_4.

but poor response to chloride ions. The selectivity of the membranes for the ions nitrate, sulphate and chloride was very poor. The introduction of O-nitrophenyl-ω-undecylenyl ether groups in the polymer, either as entangled solvent mediator or covalently bound to the polymer structure, enhanced the response of the membranes to chloride ions. The mediating molecules did not enhance the selectivity of the membranes to chloride or nitrate.

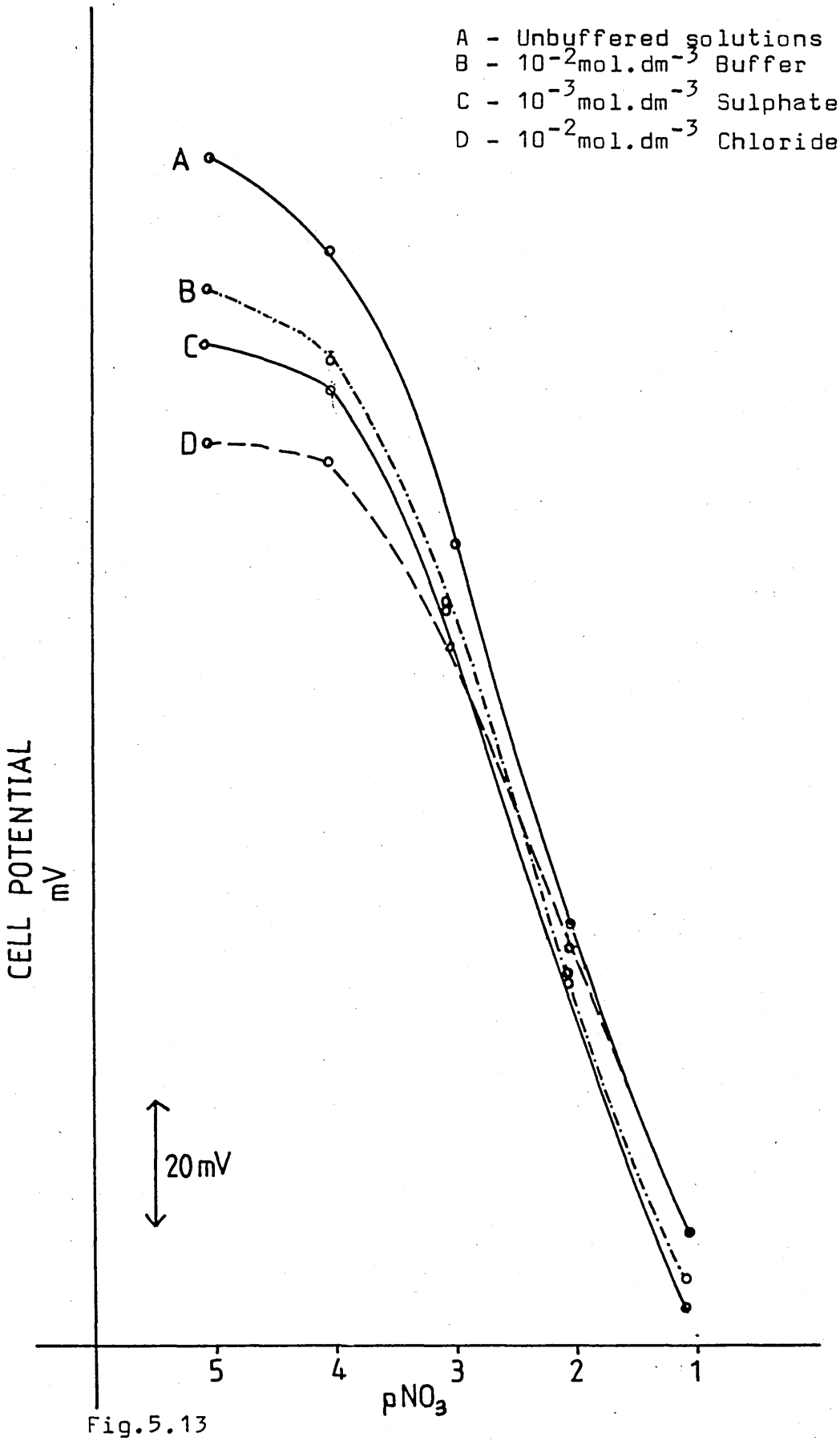


Fig.5.13
The araldite Membrane

5.6 The Araldite Electrode

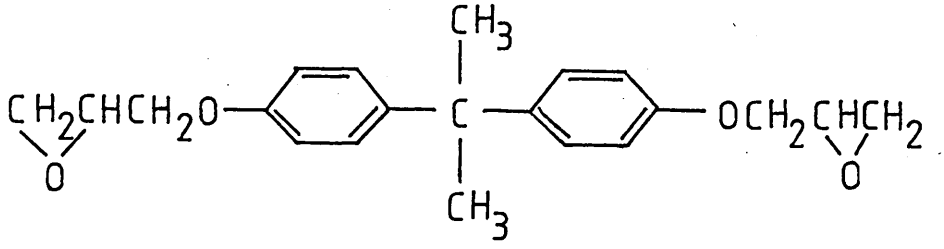
The membranes prepared in the early part of this work were evaluated using an "in house" design electrode body, Section 3.2.1.2, Figure 3.2.

Interchangeable sensor units were constructed by attaching the polymer to PVC tubing using an epoxy resin adhesive. To examine the inertness (or otherwise) of the epoxy resin adhesives, sensor units were constructed from cross-linked SBS membranes prepared without QAS. These membranes were conditioned and found to show very little response to nitrate solutions; 29mV change in potential over 4 decades. The epoxy resin was also evaluated for nitrate response. Membranes were prepared by spreading the mixture of adhesive and hardener, which form the epoxy resin (Araldite, Ciba Geigy Plastics and Additives Company, Duxford, Cambridge), evenly over a film of cellophane. The adhesive was cured for 24 hours at room temperature and sensor units were then prepared (as described previously, Section 3.2.1.3), and conditioned. These Araldite membranes showed no response after an initial conditioning of 24 hours, but after two weeks conditioning a Nernstian response to nitrate solutions was found in the range 10^{-1} to 10^{-4} mol dm^{-3}. The membranes suffered little interference from 10^{-3} mol dm^{-3} buffer or sulphate solutions, but 10^{-3} mol dm^{-3} chloride solutions caused interference below 10^{-2} mol dm^{-3} nitrate as shown in Figure 5.13. The response of the membranes was stable and

reproducible and the response times equivalent to SBS membranes. These Araldite membranes were found to have useful lifetimes of no more than 2 months.

A brief literature survey revealed the use of epoxy resins as the supporting matrix in a number of membranes. Araldite resin was used to support a nitron nitrate precipitate in the preparation of a membrane electrode[118]. This nitron electrode showed linear response to nitrate in the range 10^{-1}-10^{-4} mol dm^{-3} with a slope of 50mV. An araldite based membrane has been prepared from crystalline antimonic (V) acid[119]. Antimonic acid is a cation exchanger which shows selectivity for cations with a crystal ionic radii of approximately 0.1nm. The electrode was expected to be selective for certain anions, but actually showed a near-Nernstian response to nitrate. The electrodes were conditioned in 0.1M salt solution for 15 days. A coated-wire ion-selective electrode was prepared[120] from a liquid ion-exchanger and an epoxy resin gave a Nernstian response to nitrate.

Commercial epoxy resins[121] are based on the diglycidyl ether of bisphenol A(2) and its oligomers:-



(2)

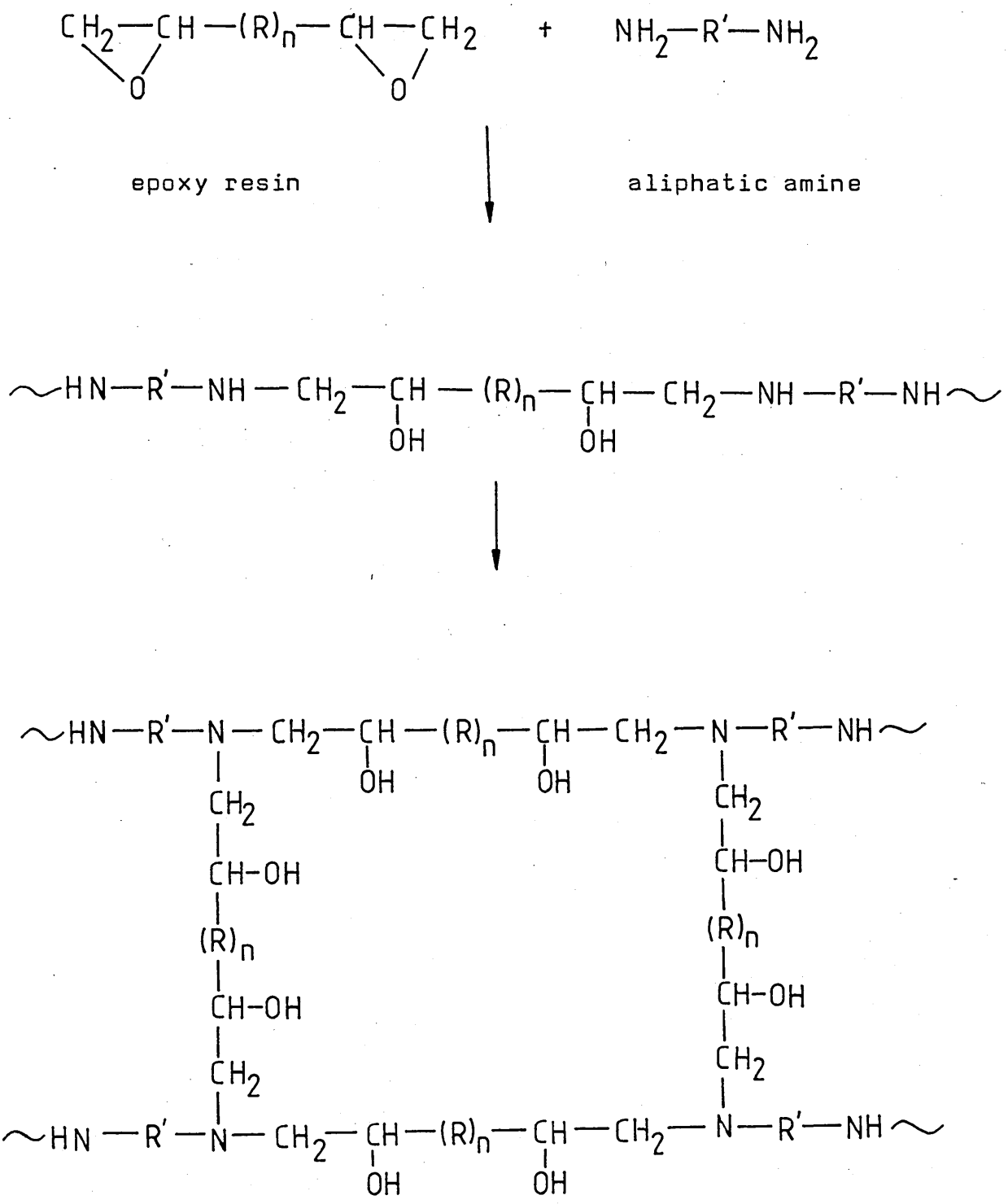


Fig. 5.14
The reaction of an epoxy resin with an aliphatic amine hardener.

The essential components are an organic molecule containing two oxirane groups, e.g. (2) and a curing agent able to produce linear polymerisation or cross-linking by reaction with these groups. The curing agent is commonly an amine which is usually present at 5 to 10 parts per 100 parts of resin. Aliphatic amines act rapidly at room temperature and are the most important group of hardeners for epoxy resins. The titratable hydrogens of the primary and secondary amine groups react with the epoxide groups until all the amines are tertiary as shown in Figure 5.14. The tertiary amines may catalyse the homopolymerisation reaction. They induce cross-linking by behaving as an anionic polymerisation catalyst but do not react directly with the epoxy resins (Figure 5.15).

The response of Araldite membranes to nitrate is less surprising when the formulation of these epoxy resins is considered. Agrawal and Abe[106], attribute the response of the antimonic acid electrode to the presence of quaternary centres in the polymer. Quaternary nitrogens may form during the hardening of the epoxy resin, but may occur in the polymer during its extended conditioning. Several commercial epoxy adhesives were used to prepare polymer membranes and similar responses were obtained. The response of conditioned epoxy resins to nitrate ions makes them unsuitable materials for ISE construction. Thus care must be taken in evaluating results from other workers who have used epoxy resins in electrode construction or membrane formulation.

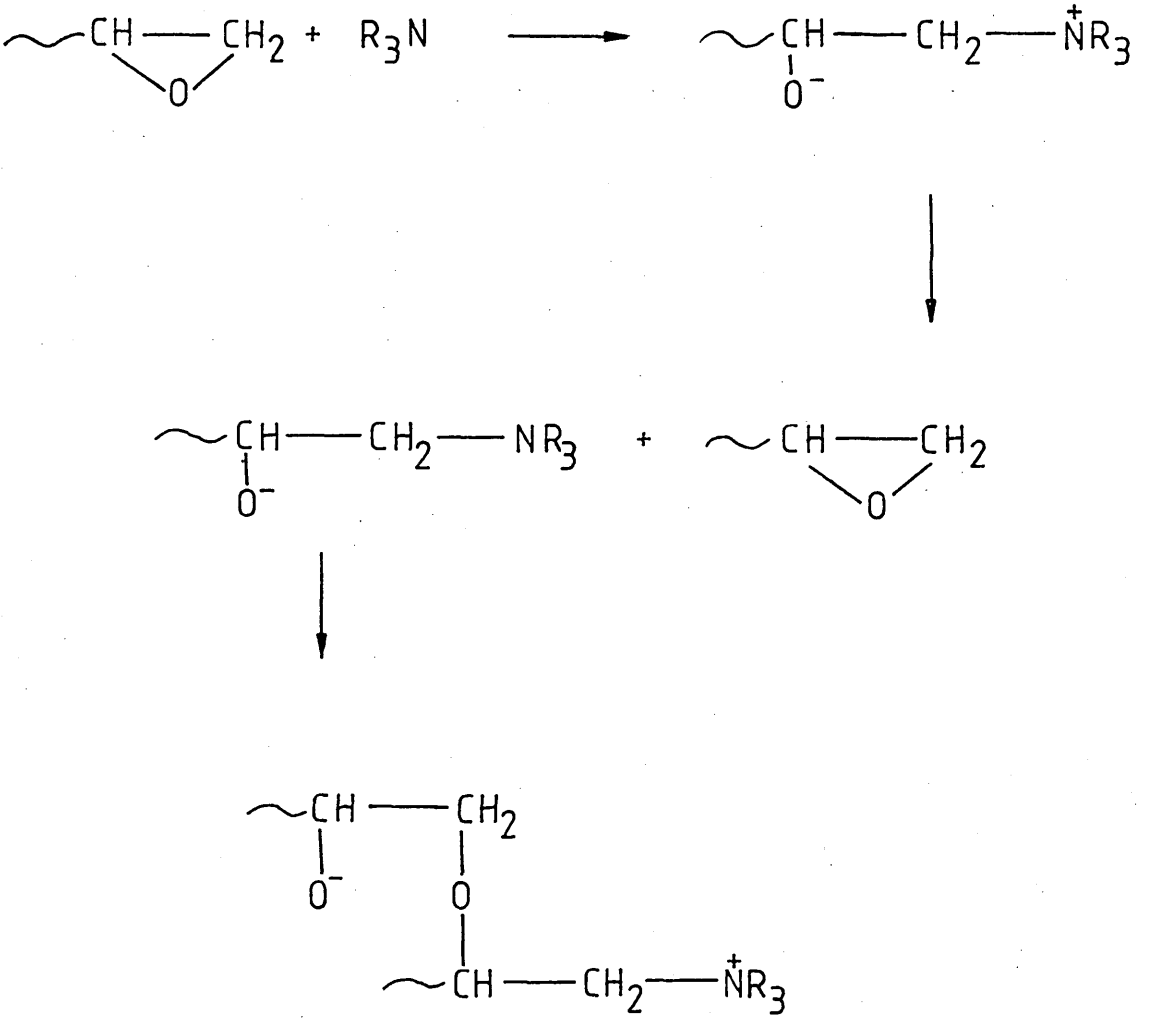


Fig.5.15
Homopolymerisation reaction catalysed by a tertiary amine group.

CHAPTER 6

Conclusion and Suggestions for Future Work

Polymer membranes with covalently bound QAS were prepared by a number of methods. The polymers were evaluated as membranes for long-lived, robust, nitrate selective electrodes. Several physical properties of the membranes were assessed including the amount of covalently bound nitrogen and the cross-linked density. The electroanalytical and physical properties of the membranes and the methods of evaluation will be reviewed here, highlighting the implication of these properties on the structure and mechanism of response of the polymer.

6.1 The Cross-linked Density Calculations.

The cross-linked density of the polymer membranes was calculated from equilibrium swelling measurements using the Flory-Rehner equation 3-16, as described in Section 3.3. A number of approximations to the standard method[108] were used and the influence of these on the final results will now be discussed.

6.1.1 The Equilibrium Swollen Weight.

The swollen weight of the polymer was determined by a single measurement for each sample, after immersion in heptane for 24 hours. The equilibrium swollen weight is determined by cycles of swelling and drying until a constant weight of dry sample is achieved. The solvent removes all uncross-linked material from the polymer, hence the final swollen weight is determined only by the interaction of the

cross-linked matrix with the solvent. The inaccuracy introduced into this work, by adopting a less rigorous approach, will be greatest for polymers with low levels of cross-linked material and therefore high levels of uncross-linked material. Any residual uncross-linked material in the polymer will effect the interaction of the cross-linked matrix with the solvent. Polymers with low levels of cross-linked material exhibit the highest swollen weights. The parameters which reflect the properties of the matrix are V_2 (equation 3-20) the volume fraction of cross-linked material, and s (equation 3-19) the weight of swollen material expressed as a percentage of the original weight. The V_2 and s values for a range of master membranes are shown in Table 6.1 along with other properties of the polymers. The results which are expected to be least accurate are those for polymers with low V_2 and high s values.

6.1.2 The Polymer Solvent Interaction Parameter.

The calculation of cross-linked density using equation 3-18 requires the polymer-solvent interaction parameter

$$N = -\frac{(\ln(1-V_2)+V_2+\mu V_2^2)}{V_1(V_2^{1/3}-V_2/2)} \qquad (3\text{-}18)$$

The polymer solvent interaction parameter $\mu = 0.589$ for heptane with SBS polymer[109] was used for the initial calculations. An exact parameter could not be derived from the

Table 6.1

Cross-linked density parameters

Master Membrane	QAS	% Nitrogen[a] w/w	s Swollen Weight %	V_2	ρ_2 g.cm^{-3}	Cross-linked Density Moles cross-links cm^{-3}
tBHPA	TAAB	0.10[b] 0.29 0.10	113 144 146	0.33 0.27 0.27	1.24	8.28×10^{-5}
tBHPB	TAAB	0.06 0.06 0.15	84 43 34	0.49 0.55 0.38	0.85	4.82×10^{-4}
tBHPC	DADMAC	0.07[b] 0.37 0.31	1.25 205 207	0.40 0.28 0.28	0.83	1.17×10^{-4}
tBHPD	TAMAB	0.20 0.38 0.06	122 183 178	0.37 0.28 0.29	0.94	1.04×10^{-4}
tBHPE	TAAB	0.05[b] 0.15 0.16	155 115 134	0.31 0.37 0.33	1.00	1.14×10^{-4}
tBHPF	TAAB	0.17[b] 0.08 0.59	78 777 84	0.50 0.50 0.48	0.89	5.68×10^{-4}
tBHPG	DADEAC	0.51[b] 0.67 0.49	311 304 300	0.17 0.18 0.18	0.96	1.68×10^{-5}
tBHPH	TAEAB	0.25 0.30 0.24	234 245 226	0.24 0.23 0.25	0.92	4.34×10^{-5}

Master Membrane	QAS	% Nitrogen[a] w/w	Swollen Weight %	V_2^s	ρ_{2} g.cm^{-3}	Cross-linked Density Moles cross-links cm^{-3}
tBHPH (REPEAT)	TAEAB	0.26 0.29 0.31	449 571	0.14 0.11	0.95	5.89×10^{-6}
MAY8	TAEAB	0.37 0.26 0.65	850 1166 964	0.07 0.06 0.07	0.99	8.5×10^{-7}
MAY9	TAEAB	0.38 0.68 0.37	425 425 390	0.15 0.15 0.16	0.86	9.3×10^{-6}
MAY10	TAEAB	0.29 0.54 0.30	534 474 395	0.11 0.13 0.15	0.98	5.89×10^{-6}
JUNE1	TAAB	0.33 0.31 0.20	500 439 430	0.14 0.15 0.16	0.86	9.30×10^{-5}
JUNE3	TABAB	0.30 0.34 0.50	252 252 262	0.22 0.22 0.21	0.99	3.25×10^{-5}
JUNE4	ATEAB	0.65 0.46 0.38	275 237 264	0.20 0.22 0.21	1.00	2.18×10^{-5}
JUNE7	DADEAB	0.44 0.52 0.46	372 353 379	0.16 0.17 0.16	0.97	1.15×10^{-5}
JUNE8	DADEAC	0.08 0.52 0.09	486 472 431	0.13 0.13 0.13	0.93	5.89×10^{-6}

er Membrane		o 1 rogen w/w	wo en Weight %	V_2	ρ_2 g. cm^{-3}	Cross-linked Density Moles cross-links cm^{-3}
MED2	TAEAB	0.31 0.13	742 809 744	0.12 0.12 0.12	0.64	4.57×10^{-6}
MED3	TAEAB	0.41 0.05 0.02	932 908 964	0.12 0.12 0.12	0.54	4.57×10^{-6}
MED4	TAEAB	0.62 0.40 0.56	377 3280 3690	0.17[b] (0.02) (0.02)	0.87	1.39×10^{-5} (2×10^{-8})
MED5	TAEAB	0.40 0.29 0.22	114 170 135	0.34 0.26 0.30	1.15	9.3×10^{-5}
SBS CROSS-LINKED - SAMPLE		-	823 944 834	0.06 0.06 0.06	1.22	5.3×10^{-7}
SBS CROSS-LINKED - SAMPLE		-	104 94 75	0.40 0.42 0.50	0.99	3.14×10^{-4}

a. Kjeldahl Analysis after solvent extraction.
b. Polymers Analysed without extraction.
ρ_2. Density of the Polymer

TAAB - Tetra-allylammonium Bromide.
DADMAC - Diallyldimethylammonium Chloride.
TAMAB - Triallylmethylammonium Bromide.
DADEAC - Diallyldiethylammonium Chloride.
TAEAB - Triallylethylammonium Bromide.
TABAB - Triallylbutylammonium Bromide.
ATEAB - Allyltriethylammonium Bromide.

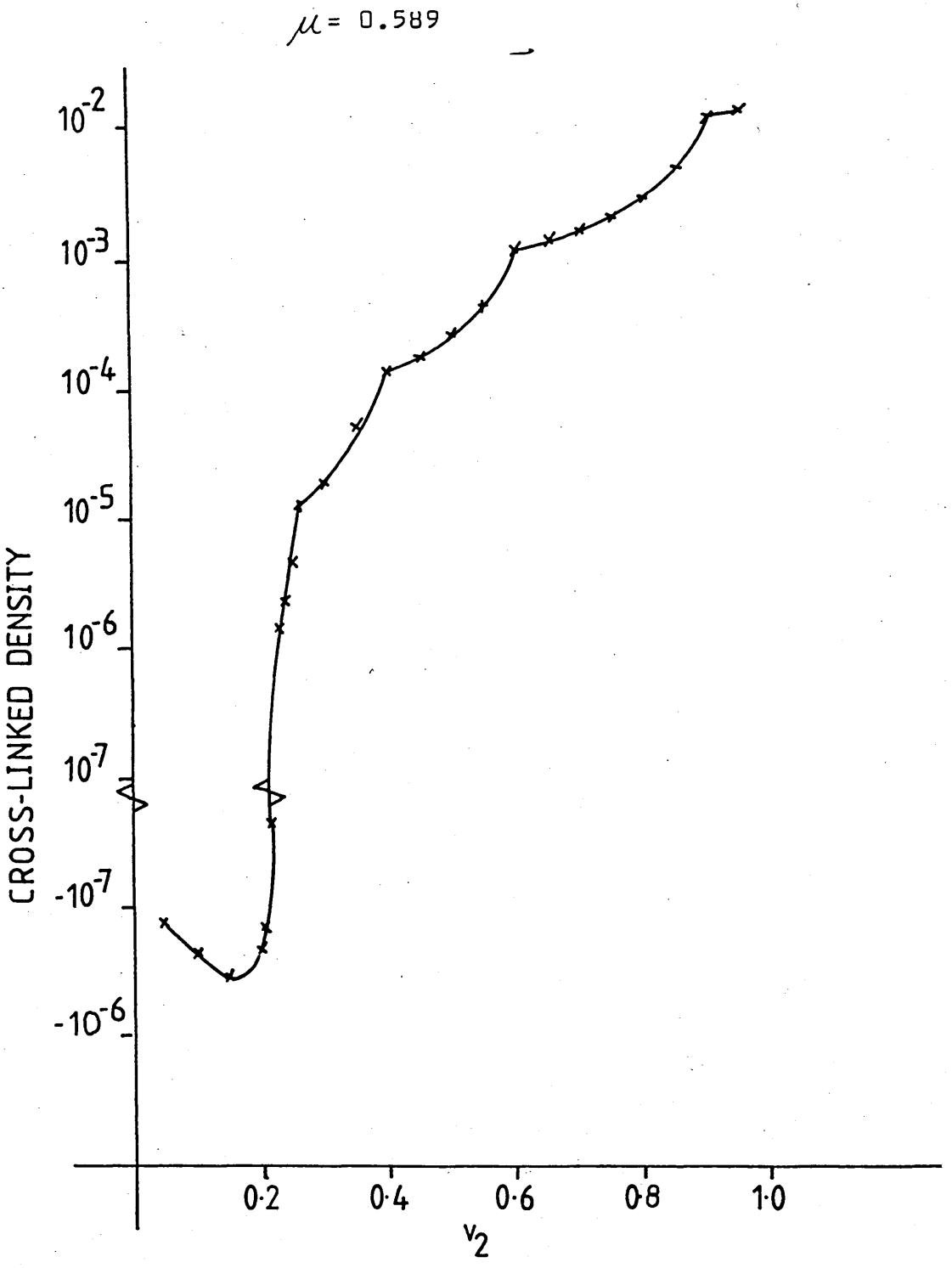


Fig.6.1
The relationship between v_2 and cross-linked density defined by equation 3-18 when μ =0.589.

literature because of the unique nature of the polymers. For accurate work a parameter for each polymer formulation would be required because of the variation in type and amount of QAS and also the addition of mediating materials to some membrane formulations.

The influence of the value of μ on the equation 3-18 was studied using the program shown in Appendix 2. The relationship expressed by equation 3-18 was found to break down at low V_2 values, which indicates that below a critical V_2 value the polymers are not considered cross-linked. The cross-linked density and V_2 values for $\mu = 0.589$ are shown in Appendix 2 and the relationship between V_2 and cross-linked density is illustrated by Figure 6.1. Many of the polymer membranes of interest in this study were found to have very low levels of cross-linked material and meaningful cross-linked density could not be determined from equation 3-18 using the polymer solvent interaction parameter for SBS polymer.

The relative cross-linked density of the polymers was required for comparison of the properties of the different polymer formulations and the electroanalytical properties of the resulting master membranes. In order to derive a range of relative cross-linked density values a number of μ values were substituted into equation 3-18 and the cross-linked density as a function of μ was followed using the program shown in Appendix 2, when $\mu = 0.5$ a range of positive

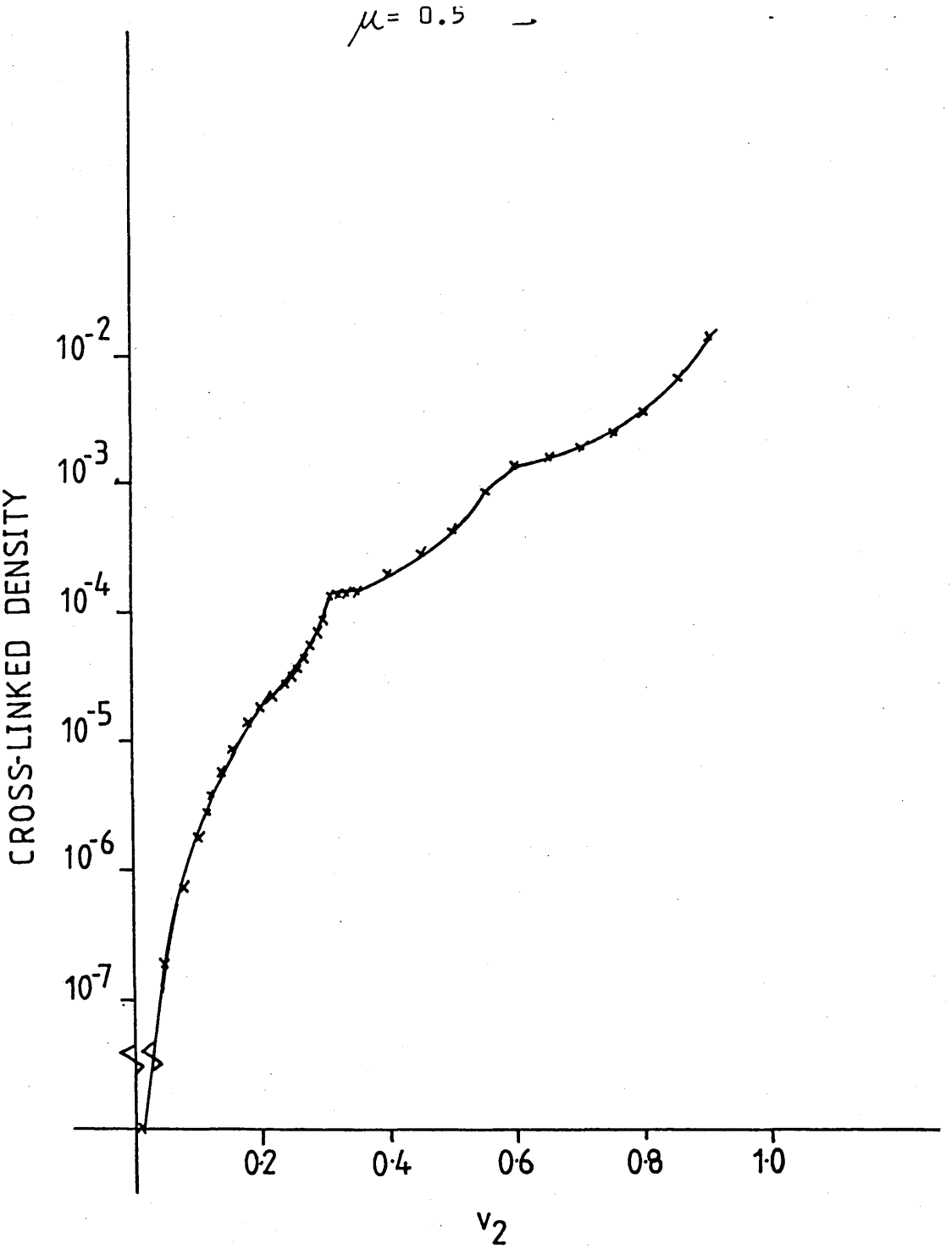


Fig.6.2
The relationship between v_2 and cross-linked density defined by equation 3-18 when μ=0.5.

cross-linked density results was obtained as shown in Appendix 3. The relationship between V_2 and cross-linked density for μ = 0.5 is shown in Figure 6.2.

Adjusting the polymer solvent interaction parameter to obtain a useful relationship between V_2 and cross-linked density was considered to be justified by the results of qualitative tests for cross-linking. When μ = 0.589 the relationship between V_2 and cross-linked density fails below V_2 = 0.23. This breakdown implies that SBS with a volume fraction of elastomer less than 0.23 is not cross-linked. An 'uncross-linked' polymer remains soluble in at least one solvent. The polymers prepared with QAS as shown in Table 6.1 were considered to be cross-linked because of their insolubility in THF after curing. Therefore, although the volume fraction of cross-linked material is low, it should be possible to obtain a cross-linked density value for each polymer.

The cross-linked density of SBS polymer cured with tBHP initiator was 3.74×10^{-4} moles of cross-links cm^{-3} calculated with the adjusted μ value compared to 2.24×10^{-4} moles of cross-links cm^{-3} calculated with the μ value for SBS in heptane.

The values for V_2 and the cross-linked density of the master membranes were compared with the relevant value for a sample of SBS (μ = 0.50) which was not cross-linked. With the exception of MAY8 all the master membranes were found to have higher V_2 values than uncross-linked SBS. The inaccuracy of these determinations is expected to be greatest for very

low V_2 values, and this is reflected in the results for MAY8. Comparison of V_2 values for MAY8 with uncross-linked SBS, implies that MAY8 was not cross-linked, however a qualitative solubility test showed MAY8 was cross-linked but SBS was soluble.

These cross-linked density measurements could not be used for comparison with published data. Comparison with SBS cross-linked density, which is expected to be more accurate result, showed that the measurements with the exception of MAY8 were of the right order of magnitude. The calculation of cross-linked density could be used most effectively for the comparison of physical and electroanalytical properties of a range of chemically identical polymers, for which an accurate μ value could be determined. However these cross-linked density results did provide a means of comparing the physical properties and therefore possible chemical structures of the polymers prepared in this work, for which other methods of probing the structure were unsuitable.

6.2 The Polymer Structure

The structure of the cross-linked SBS polymer with covalently bound QAS is difficult to study because of the low level of QAS in the polymer matrix. Digestion of the solid polymer is required for analysis because it is rendered insoluble by cross-linking. The allyl unsaturation was indistinguishable from the unsaturation in the polymer when thin polymer films were studied. A suitable technique

with which to study QAS bonding to the SBS matrix would be n.m.r. using a solid sample, but suitable instrumentation was unavailable. However, the results of Kjeldahl analysis and the cross-linked density of the polymers were of use in comparing different ideas for the polymer structure.

The properties of allyl substituted QAS were discussed in Section 2.2. These QAS, depending upon the number of allyl substituents, form linear water soluble polymers or cross-linked insoluble polymers predominantly by a cyclopolymerisation mechanism. The stereochemistry of the QAS within the polymer matrix will depend upon the extent of allyl substitution and subsequent covalent attachment.

Mono-allyl QAS may only form a single covalent attachment (and do not form homopolymers), diallyl, triallyl and tetra-allyl QAS may form multiple covalent attachment which could be intermolecular or intramolecular with respect to the SBS matrix and could involve a cylcopolymeriation step.

The SBS polymer showed insignificant cross-linking when cured with low levels <5% tBHP initiator, but when a QAS was present a cross-linked matrix resulted (Section 4.4). Therefore the QAS was thought to form the cross-links by covalent attachment to SBS polymer chains, as shown in Figure 6.3. An increase in cross-linked density was expected with increasing covalent attachment of QAS. The cross-linked density and the average covalently bound nitrogen (%N w/w by Kjeldahl analysis) for a range of polymers are shown in Table 6.2.

Table 6.2

Comparison of Cross-linked Density with the Amount of Covalently Bound Nitrogen.

Master Membrane	Average[a] %N w/w	Cross-linked Density (Moles Cross-links cm^{-3})	Number (For Fig.6.4)
tBHPA	0.16[b]	8.28×10^{-5}	16
tBHPB	0.09	4.82×10^{-4}	17
tBHPC	0.25[b]	1.17×10^{-4}	18
tBHPD	0.21	1.04×10^{-4}	19
tBHPE	0.12[b]	1.14×10^{-4}	20
tBHPF	0.28[b]	5.68×10^{-4}	21
tBHPG	0.56[b]	1.68×10^{-5}	1
tBHPH	0.26	4.34×10^{-5}	2
tBHPH (REPEAT)	0.29	5.89×10^{-6}	3
MAY8	0.43	8.5×10^{-7}	4
MAY9	0.48	9.3×10^{-6}	5
MAY10	0.38	5.89×10^{-6}	6
JUNE1	0.28	9.3×10^{-6}	10
JUNE3	0.38	3.25×10^{-5}	11
JUNE4	0.50	2.78×10^{-5}	12
JUNE7	0.47	1.15×10^{-5}	13
JUNE8	0.23	5.89×10^{-6}	14
MED2	0.22	4.57×10^{-6}	15
MED3	0.16	4.57×10^{-6}	7
MED4	0.16	1.39×10^{-5}	8
MED5	0.30	9.3×10^{-5}	9

a. Kjeldahl Analysis after Solvent Extraction.

b. Polymers Analysed without Extraction.

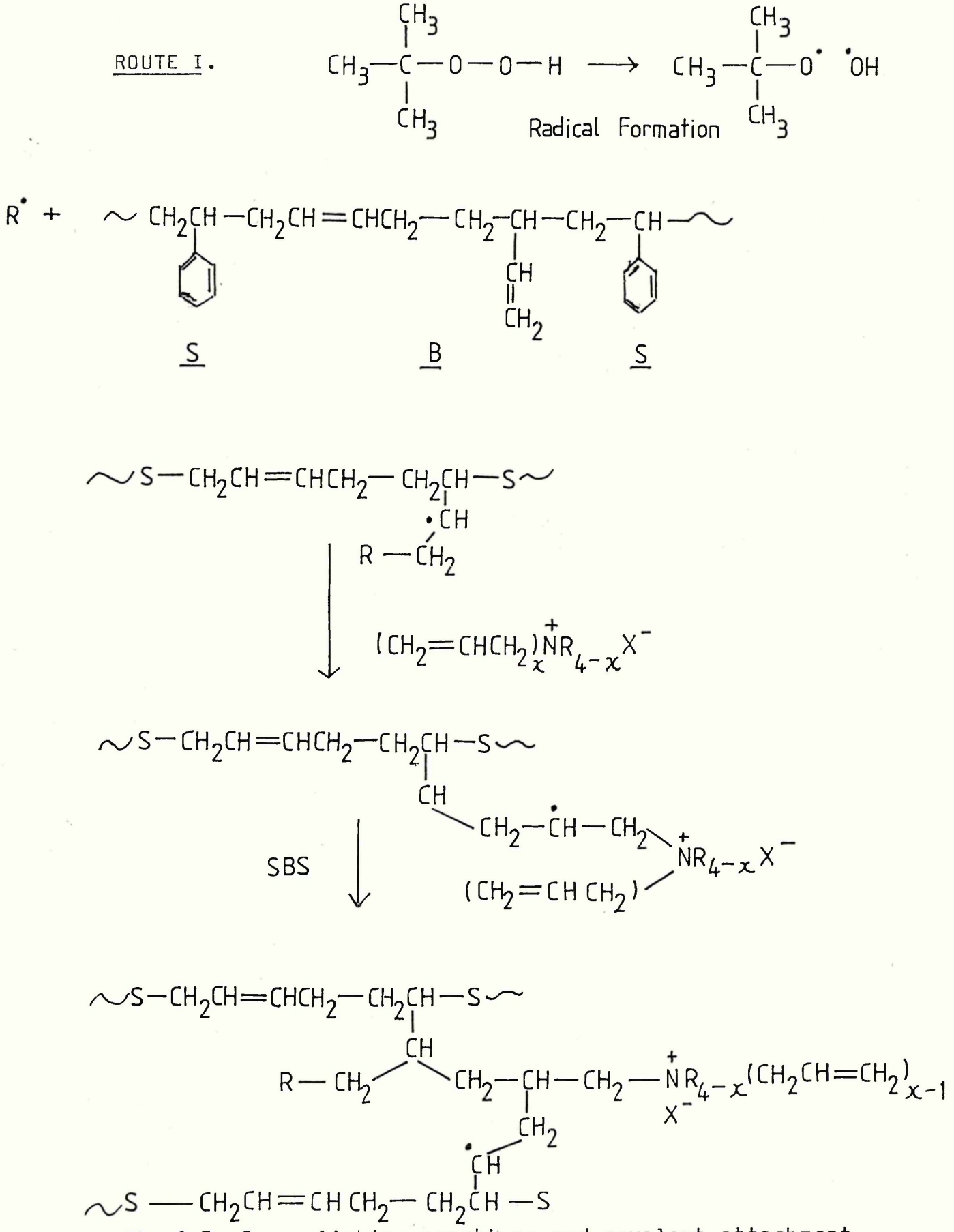


Fig.6.3 Cross-linking reactions and covalent attachment of allyl substituted quaternary ammonium salts.

ROUTE II.

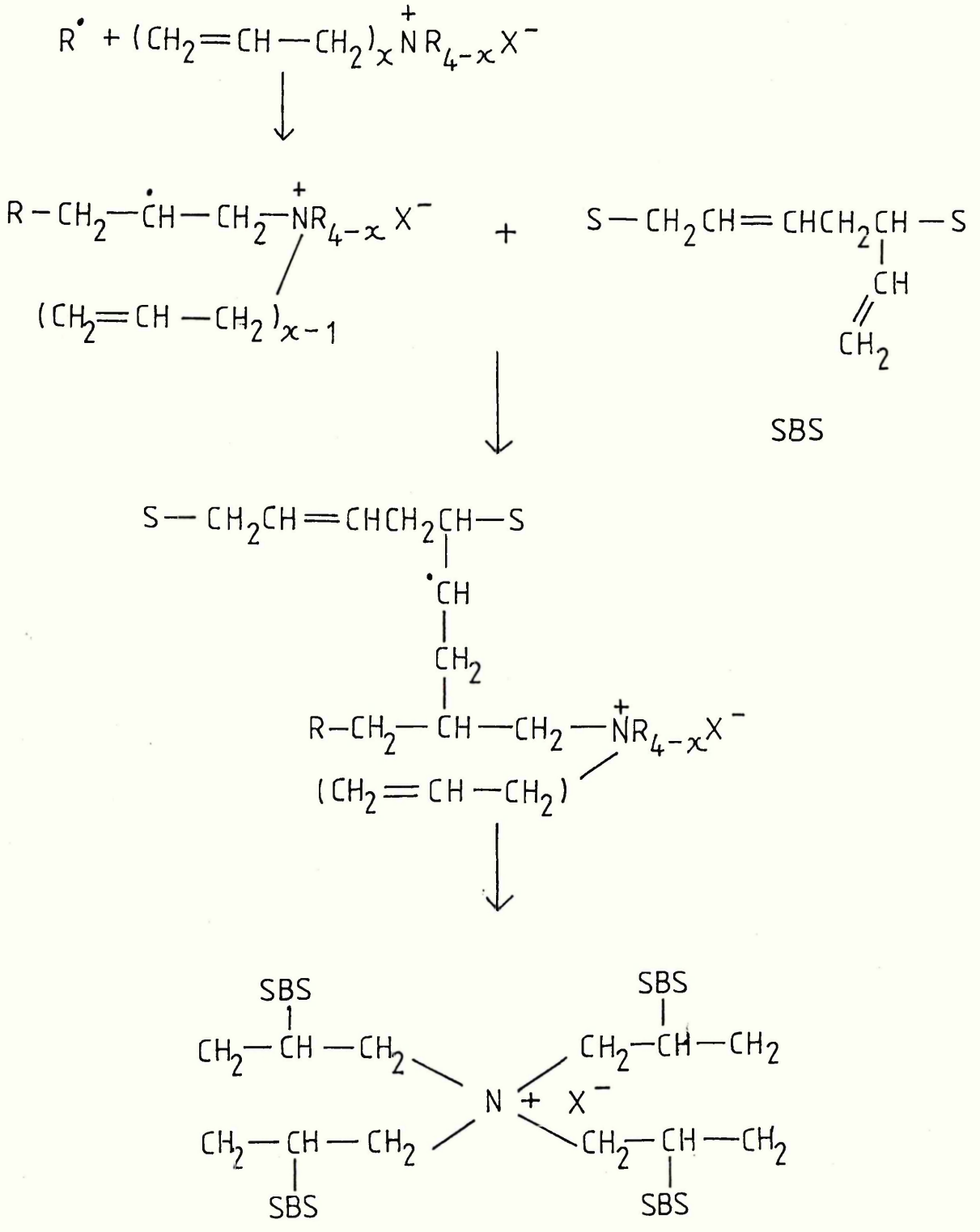


Fig.6.3 (continued) Cross-linking reactions and covalent attachment of allyl substituted quaternary ammonium salts.

ROUTE III.

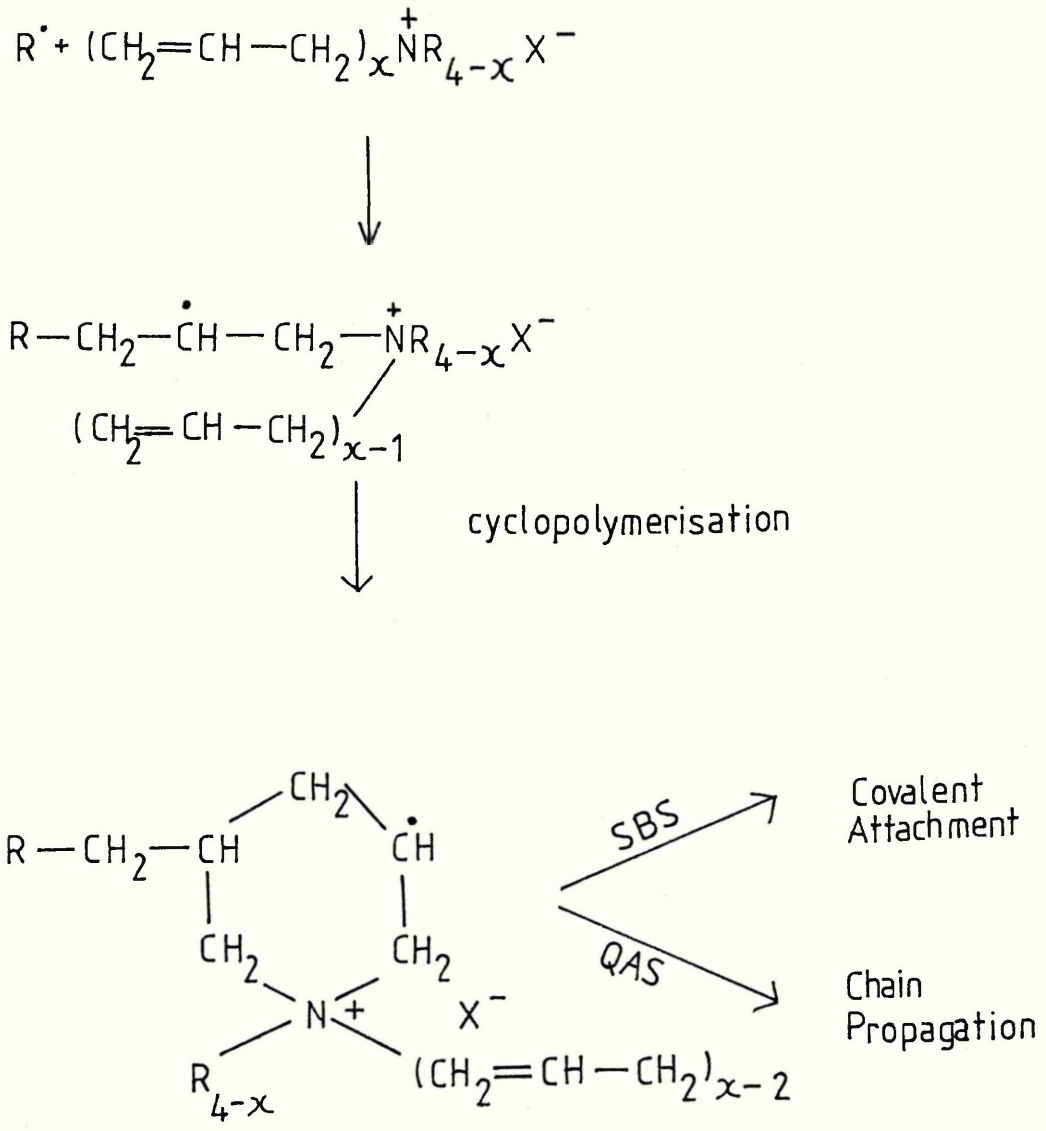


Fig.6.3 (continued) Cross-linking reactions and covalent attachment of allyl substituted quaternary ammonium salts.

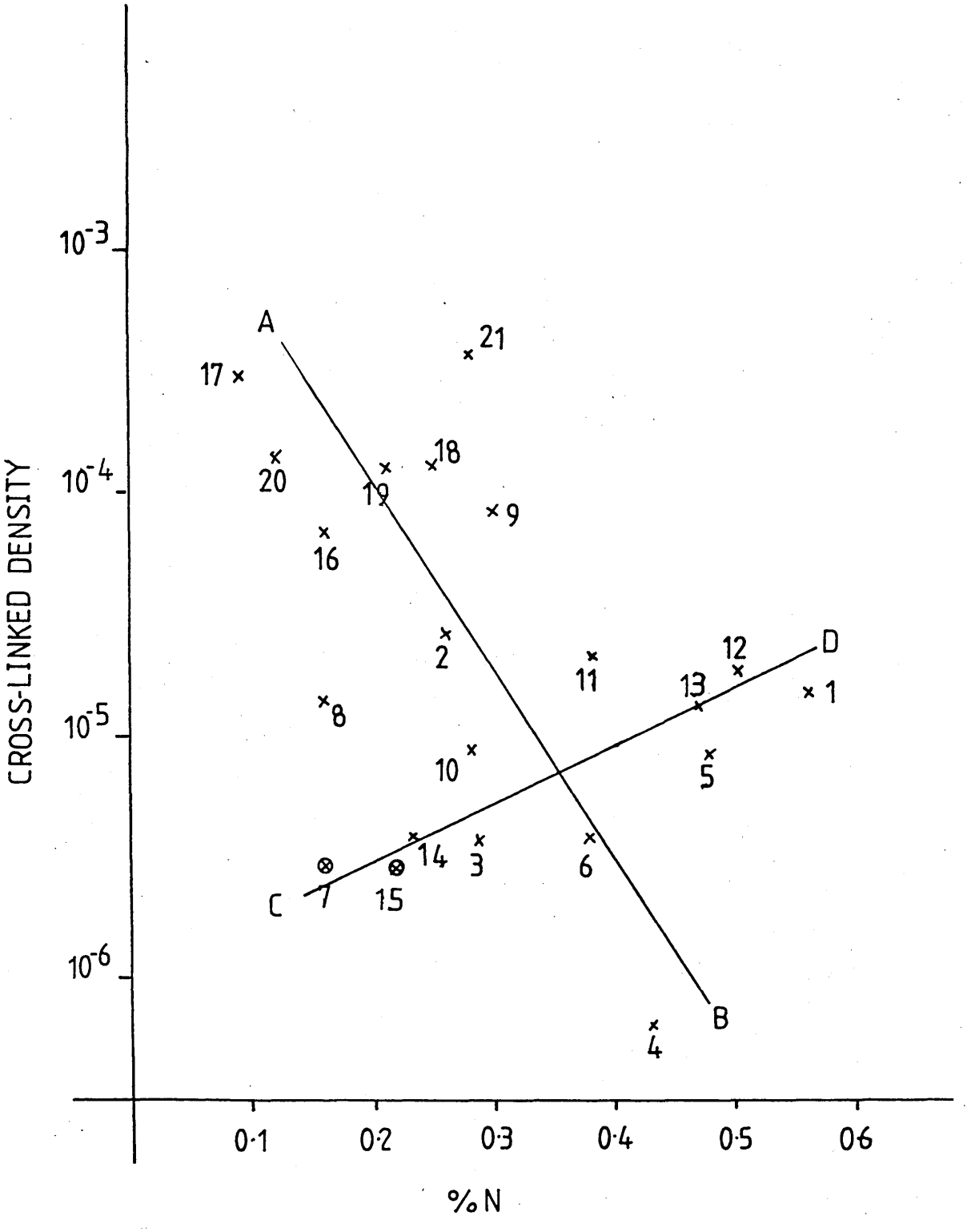


Fig.6.4
The relationship between cross-linked density and covalently bound nitrogen.

The relationship between cross-linked density and covalently bound nitrogen is shown in Figure 6.4. The points are widely scattered, possibly because no account has been taken of the amount of initiator or the presence of mediator in the polymers, both will influence cross-linking. The expected trend of increasing cross-linked density with increase in covalently bound nitrogen is represented by line CD. However, many of the points are accounted for by line AB, which represents a decrease in cross-linked density with increase in covalently bound nitrogen. These two opposing trends and their possible consequence for the polymer structure are reviewed below.

Polymers with high levels of covalently bound nitrogen show lower than expected cross-linked density, therefore a different mechanism of QAS attachment could be taking place when high percentages of nitrogen are present. It is possible that covalent attachment of QAS occurs, at both high and low levels of covalently bound nitrogen, without promoting effective cross-linking and that any cross-linking which is observed is caused by tBHP initiator. However this is inconsistent with the observed behaviour of SBS cured with tBHP in the absence of QAS.

An alternative mechanism for the increased covalent attachment of QAS without increased effective cross-linking could involve homopolymerisation of the QAS within the SBS matrix. When high concentrations of QAS are present in the

polymer matrix the dominant reaction could be cyclopolymerisation of the QAS and thus chain propagation by reaction with a neighbouring QAS. The chain propagation step could begin and/or terminate with an SBS linkage, and covalent attachment of the propagating chain could also occur through the additional unsaturation in the triallyl and tetra-allyl derivatives.

The formation of an independent homopolymer (unattached to the SBS matrix) is a further possibility. However this is considered to be unlikely for triallyl QAS when the results of cross-linked density and Kjeldahl analysis are taken into account. If such a polymer formed from diallyldiethylammonium bromide or chloride and thus was only entangled within an SBS matrix, methanol extraction prior to Kjeldahl digestion would be expected to remove substantial amounts of the linear methanol soluble polymer. However, the master membrane JUNE7 was found to contain 90% of the expected nitrogen, although a wide variation in the %N for JUNE8 was found as shown in Table 4.6. Opaque areas were observed in membranes prepared with DADEAC after oven curing, these opacities did not appear to be precipitated QAS. However the inhomogeneous nature of the polymer could result from homo-polymerisation of DADEAC, QAS. If the homopolymerisation reaction rate is rapid compared to the rate of reaction with SBS, the linear QAS polymer could form in isolation. The Kjeldahl analysis of the polymer identified areas which were

depleted of nitrogen, possibly because the linear, water soluble, QAS, polymer was leached from the SBS matrix. The rate of polymerisation of quaternary ammonium bromides is less rapid than the chlorides[94], and may be similar to the rate of their reaction with SBS. The bromide salts would form more cross-links with SBS than chlorides under these restrictions. The triallyl QAS are more likely to form covalent attachment with SBS because of the additional allyl groups; it is probable that the homopolymer of these QAS would also be cross-linked and insoluble.

The master membranes tBHPA-F showed little or no response to nitrate solutions, this was attributed to the highly cross-linked nature of the membranes and the relatively low levels of QAS they contained compared to the polymers tBHPH which showed superior electro-analytical properties. The poor response of the membranes may also result from insufficient QAS being present to form a conductive network within the polymer matrix Perhaps the formation of areas of QAS polymer within the SBS matrix, but also covalently bonded to it, are essential to the electroanalytical behaviour of the membrane. There may be an optimum level of QAS at which the type of polymerisation changes; the amount of QAS may control both the amount of covalently bound nitrogen and the type of covalent attachment.

The master membrane JUNE4 was prepared with ATEAB, a mono-allyl QAS which would not be expected to form homopolymers. Although the master membrane was found to have a high level of covalently bound QAS, and low conditioned resistance the initial response of the membrane was sub-Nernstian and deteriorated rapidly. The cross-linked density of the polymer was similar to other membranes with equivalent levels of QAS, but was expected to be significantly lower because the mono-allyl QAS was not expected to form multiple covalent attachment. The single allyl group probably reacts with SBS as shown in Route II or Figure 6.3. The cross-linked density although higher than expected, was not sufficiently high to prohibit response when compared with tBHPA-F. The poor response of the master membrane JUNE4 may result from the isolated covalent attachment of QAS within the polymer matrix, a conductive network may not be formed.

The membranes represented by line CD in Figure 6.4, with the exception of MED2(15) and MED3(7) showed the most encouraging electroanalytical properties. These polymers showed the expected trend of increasing cross-linked density with increasing covalently bound nitrogen. If the type of polymerisation and cross-linking does depend upon the amount of QAS present, then the characteristics of polymers prepared with greater than 15% QAS should be examined. The type of QAS should be limited to triallyl quaternary ammonium bromide which produce the most homogeneous membranes.

The preparation of polymer membranes with covalently bound QAS requires further investigation to optimise the formulation and perhaps improve the electroanalytical properties of the membranes. When a homogeneous polymer has been identified with high levels of covalently bound nitrogen, a second modification to the structure of the polymer could be investigated. The polymers could be further cross-linked using tBHP initiator solution and curing at 60°C. A single homogeneous membrane could be treated after solvent casting to produce polymer samples with a range of cross-linked density.

6.3 Selectivity

The QAS described in Section 2.2.1 provided a range of sensors. The variation in the number of allyl substituents was expected to give variations in stereochemistry between mono, di, tri and tetra-allyl QAS, if the maximum covalent attachment occurred. The remaining substituents on the quaternary nitrogen were alkyl groups and varied in the length of the carbon chain C_1-C_4. A range of QAS with longer alkyl substituents would have been preferred as sensors to provide a more hydrophobic polymer, but their preparation was not achieved. The quaternary ammonium salts prepared for this work were used in a series of master membranes to provide equivalent amounts of quaternary nitrogen in each formulation in order to compare the performance of the QAS as a nitrate sensor. The formulations are shown in Table 2.10. A poor response to nitrate was found for diallyl

QAS and membranes prepared with ATEAB, TAMAB and TAPAB. The polymers prepared with these QAS were found to have low but sometimes linear responses to nitrate often followed by deterioration of the initial response. The most sensitive membranes were prepared from the QAS, TAAB, TABAB and TAEAB. These QAS showed Nernstian response from 10^{-1} to 10^{-4} mol dm^{-3} nitrate solution with decreased response to 10^{-5} mol dm^{-3}. The selectivity of these QAS varied with the actual formulation of the polymers, for example the amount of QAS, and initiator. The range of QAS were expected to show similar response to nitrate but some variation in selectivity was expected. However a range of sensitivity to nitrate, which could result from the type of polymerisation within the SBS matrix, was found.

The membranes prepared in this work, by covalent attachment of QAS to SBS polymer, were inferior in selectivity to the Philips IS56 membrane E.I.L. (liquid membrane) electrode and Corning ion-exchanger in PVC.[64] The selectivity coefficients $k^{Pot}_{NO_3Cl}$ are shown in Table 6.3. The poor selectivity limits the possible applications of the electrodes produced in this work. The robust membranes showed long lifetimes and were intended for continuous monitoring applications, or hostile environments. However, such conditions will provide a wide range of interfering ions and the SBS membranes showed poor response in solutions of common ions such as chloride and sulphate, phosphate buffer also suppressed nitrate response.

Table 6.3

Selectivity Coefficients

Membrane	Sensor	$K^{Pot}_{NO_3,Cl.}$ Selectivity Coefficient	Method and Solution[b]
M1	TAEAB[a]	1.41×10^{-1}	10^{-3} mol dm^{-3}
tBHPH	TAEAB[a]	5.62×10^{-1}	
MAY10	TAEAB[a]	7.94×10^{-2}	
MED4	TAEAB[a] with o-nitrophenyl -w-undecylenyl ether	1.12	
ARALDITE	Possibly a quaternary ammonium salt.	2.24×10^{-2}	
E.I.L. LIQUID MEMBRANE	E.I.L. Sensor in o-nitrophenyl-w-undecylenyl ether	7×10^{-3}	
PHILIPS PVC 1S561 NO_3	QAS	10^{-2}	10^{-1} mol dm^{-3} (separate solutons)
PVC ELECTRODE[64] WITH CORNING ION-EXCHANGER 477316	tri-dodecylhexadecyl ammonium nitrate in n-octyl o-nitrophenyl ether	5×10^{-3}	5×10^{-1} mol dm^{-3}

a. Sensor is thought to be $TAEA^+NO_3^-$ after conditioning.

b. Mixed solution using 10^{-2}mol dm^{-3} chloride ion unless alternative solution or method is specified.

The sub-Nernstian response of all SBS membranes to dilute solutions from 10^{-4} to 10^{-5} mol dm^{-3} could result from the diffusion of conditioning solution from the polymer matrix, which would create a high local concentration of nitrate at the membrane/sample interface.

A number of membranes were conditioned in chloride or sulphate solutions. All unmediated membranes with the exception of JUNE8 which was prepared from DADEAC, produced poor response to chloride as shown in Figures 4.11 and 4.12 but two membranes showed Nernstian response to sulphate solutions as shown in Figure 5.11. However the poor selectivity of the membranes for both sulphate and chloride would prohibit their use in electrodes for these ions.

The intention of this work was to prepare a nitrate selective electrode with covalently bound sensors. A suitable polymer matrix was prepared which showed sensitivity to nitrate but poor selectivity.

6.4 Mediators for Polymer Membranes.

Mediators have been used to improve the selectivity of membranes used in ion-selective electrodes. The role of the mediator within the polymer matrix depends upon the mechanism of response which varies with the type of membrane.[123]

6.4.1 Solid Ion Exchangers

Glass electrodes and other solid-state electrodes behave as solid ion-exchange resins. The three dimensional lattice of elemental oxides which constitutes the glass membrane responds almost exclusively to cations. The outer layers of glass are

hydrated and permeable to cations and function as an ion-exchanger when the glass membrane separates solutions, with a common cation, of different concentrations. The selectivity of the membrane depends upon the mobility of the ions and the ion-exchange equilibrium between the aqueous phase and the membrane. The dynamic response time of these solid state electrodes is faster than any other type of ion-selective electrode. Charge conduction through the membranes occurs by the diffusion of charged species. However passage of H^+ does not occur in the glass pH electrode. The fast response time of the solid state electrodes is attributed to equilibration of ion-exchange occurring only at the surface; only the sensor determines selectivity.

6.4.2 Liquid Ion-Exchange.

Liquid ion-exchange membranes are composed of a water immiscible solvent with a significant concentration of an ionisable species which is insoluble in water. The liquid ion-exchanger sensors are mobile, unlike the solid ion-exchanger sites which are fixed. The selectivity of liquid ion-exchangers depends upon the partition coefficient of the ion between water and the solvent and the mobility of the dissociated ions in water. When the ion-exchanger and ion are almost completely dissociated the selectivity is determined to a large extent, by the solvent. The solvents used as mediators for liquid membranes usually have low dielectric constants; the association between the ions and the sensors is thus expected to be significant.

$$I^+ + S^- \overset{K_{IS}}{\rightleftharpoons} IS$$

K_{IS} - is the association constant.

The selectivity of the membrane for a particular ion depends upon the partition coefficient and the association constant. The dynamic response time of liquid membranes is longer than the dynamic response time for the solid ion-exchanger types because equilibration between the solution and the bulk of the membrane needs to take place.

6.4.3 Polymer Membranes.

The response time of PVC membranes is intermediate between solid and liquid ion-exchanger membranes, and permeation of ions through the bulk of the matrix has been shown to occur.[124,125,126]

The membranes prepared in this work were found to have fast response times, which were slower than solid-state electrodes, but very similar to PVC. Therefore membranes prepared in the study, like PVC membranes, are thought to be intermediate between solid-state behaviour and liquid membrane behaviour but the sensors are fixed like the glass electrode. The membranes produced from SBS polymers with covalently bound QAS probably behave as solid ion-exchangers, with ion-exchange as the dominant influence on the membrane potential. However the membranes with low cross-linking may contain aqueous solution throughout the membrane structure (water acting as solvent mediator?) and the flux of ions in the solution probably hinders response, and selectivity.

Previous work by this group showed that a calcium selective electrode prepared from SBS polymer having covalently bound phosphate sensors, showed similar response time behaviour as glass electrodes and Ca^{2+} ions did not diffuse through the bulk of the membrane[127]. The response of this calcium electrode was attributed to ion-exchange in the hydrated surface layers of the polymer. Considering the possible mechanisms of response there are a number of methods of influencing the selectivity of the SBS membranes with covalently bound QAS.

(i) A solvent-mediator with a suitable dielectric constant and partition coefficient to impart nitrate selectivity.

(ii) Modification of the polymer structure.

The first option would change the mechanism of response to that of a liquid membrane, but with fixed sites. The second option would favour a closer approach to the mechanism of response of a solid ion-exchanger.

The first option was explored using a traditional solvent mediator for nitrate electrodes, O-nitrophenyloctyl ether. The impregnation of cross-linked polymer destroyed the robust nature of the cross-linked SBS polymer. The SBS matrix does not require plasticisation, and O-nitrophenyloctyl ether acted as a plasticiser. The solvent mediator improved the selectivity of the membrane although only a fleeting study was performed before the membrane disintegrated. The response time of the membranes increased, suggesting that the mechanism of response had become equivalent to that of a liquid membrane.

The second option was explored by covalent attachment of a "mediator" with the same properties as O-nitrophenyloctyl ether, but with suitable functionality for cross-linking reactions. The covalent attachment of O-nitrophenyl-ω-undecylenyl ether to the polymer matrix with covalently bound QAS did not improve the selectivity of the polymer for nitrate. However, the sensitivity of the polymer to chloride ions was improved. The properties of O-nitrophenyl-ω-undecylenyl ether as a nitrate preferring medium were not transferred from the liquid to the solid state but modification of response was achieved.

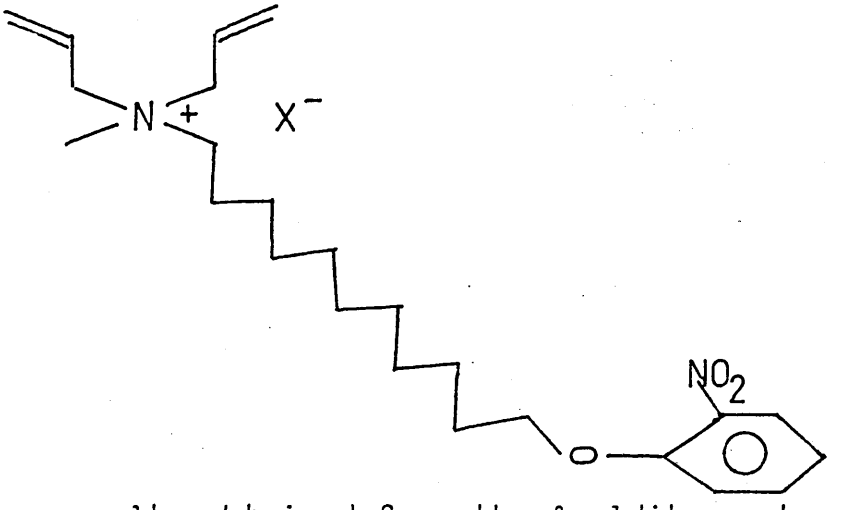
The development of liquid membrane electrodes was assisted by the established techniques of solvent extraction and measurement of partition coefficients. There is no readily available methodology or well established measurements for the development of new membrane materials which are essentially solid - i.e. tailor made polymers for individual ions.

An alternative method of modifying the polymer structure in order to influence the selectivity and favour a solid ion-exchanger mechanism would be to increase the cross-linked density. The early polymer membrane M1 (Figure 4.3) showed a different pattern of interference, similar to that shown by Araldite (Figure 5.13). The tBHP membranes showed severe interference from SO_4^{2-} (Figure 4.6). The cross-linked density of M1 was expected to be higher than the later tBHP

initiated membrane, because UV irradiation and ABIN promote SBS cross-linking. The average cross-linked density of a typical solvent cast U.V. irradiated membranes D3 was found to be 3.34×10^{-3} moles cross-links cm^{-3} (this membrane was several months old and cross-linking was probably enhanced by oxidative cross-linkages). The sensor unit M1 and the Araldite membrane were more selective for nitrate, sulphate ions and phosphate buffer solution caused only minor interferences. An increase in the cross-linked density of the matrix may have excluded these larger less mobile anions. The cross-linked density of a single master membrane could be varied after initial preparation, or even after ion-exchange in a suitable solution. The cross-linked density could be increased by treatment with tBHP initiator, UV irradiation or hot-pressing. The cross-linked density of the samples could then be compared with performance of the membranes as ion-selective electrodes. An improvement in the selectivity of the membranes for nitrate in the presence of chloride would be difficult to achieve by "tightening up" the matrix. Chloride is the smaller ion of the two and probably more mobile. The mobility would depend upon a balance between the size of the ion and its charge (charge density) which influences the hydration shell.

The polymer membranes prepared by covalently attachment of O-nitrophenyl-w-undecylenyl ether groups were more senstivie to chloride than the original polymers containing just the sensor. The covalent attachment of the mediator molecule,

modified the chemical structure of the polymer membranes. However the increased sensitivity to chloride could also have been achieved by other molecules, and covalent attachment of a range of materials to the polymer matrix. The electro-analytical properties of the modified polymer could then be studied in order to gain some understanding of the nature of selectivity in these novel membranes. Increasing the cross-linked density of the polymer with covalently bound O-nitrophenyl-w-undecylenyl ether could produce a useful chloride selective membrane. It would also be interesting to combine the properties of the QAS sensor and the mediator molecule into a single unit and study the properties of the resulting membrane:-



The interesting results obtained from the Araldite membrane stimulate a number of ideas. The selectivity of the polymer could result from the cross-linked density of the matrix and operate by size exclusion. Alternatively this polymer, like the glass or other solid state electrode, may have a structure suited to a particular ion. The general structure of Araldite

resin could be functioning as a sensor, unlike the membranes prepared in this work which have sensors attached to an inert matrix. The Araldite structure may also contain the equivalent of a solid mediator which in conjunction with sensor groups impart some selectivity to the general matrix.

6.5 Conclusion

In order to develop a long-lived nitrate selective electrode with covalently bound sensor groups to withstand hostile conditions, and which functions as a solid ion-exchanger, a more selective sensor group is required. The QAS sensors used in this work produce polymers with ion-exchange properties but negligible selectivity. The improvement of selectivity by impregnation with solvent mediators detracts from the possible lifetime of the membrane and their mechanical properties. We do not yet have sufficient undertanding of the influence of "solid" mediators on selectivity to modify the present generation of electrodes. However the SBS polymer with covalently bound QAS could eventually provide nitrate, chloride or sulphate selective electrodes if the selectivity of the membrane was suitably modified.

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APPENDIX 1

BASIC programme for the calculation of s, v and cross-linked density.

```
90  CLEAR
100  DIM MSDPO(6),SMPO(6),S(6),V2(6),XLD(6),NXL(6),MPO(6),MH2O(6),DPO(6)
110  PRINT "INPUT CODE OF MASTER MEMBRANE"
120  INPUT NAMES$
130  PRINT "INPUT NO.OF SAMPLES"
140  INPUT LIMIT
150  FOR B = 1 TO LIMIT
160  PRINT "MASS OF SWOLLEN/DRIED POLYMER"
170  INPUT MSDPO(B)
180  NEXT B
190  FOR C = 1 TO LIMIT
200  PRINT "MASS OF SWOLLEN POLYMER?"
210  INPUT SMPO(C)
220  NEXT C
225  PRINT "TEMP HEPTANE"
226  INPUT THEP
227 TH = 20 - THEP
228 P1 = 0.68376 + TH * (8.5 .* 10 ^  - 4)
240  REM  P1= DENSITY OF HEPTANE
250  GOSUB 1000
260  FOR E = 1 TO LIMIT
270 S(E) = (SMPO(E) - MSDPO(E)) / MSDPO(E)
280 V2(E) = 1 / (1 + (AVD / P1) * S(E))
281  PRINT "S FACTORS"
282  PRINT S(E)
283  PRINT "V FACTORS"
284  PRINT V2(E)
290 V1 = 147.5
300 BL = V1 * (V2(E) ^ (1 / 3) - (V2(E) / 2))
310 MU = .589
320  REM  MU IS POLYMER SOLVENT PARAMETER
325 FF = 1 - V2(E)
330 TL =  LOG (FF) + V2(E) + (V2(E) ^ 2) * MU
340 XLD(E) = ( - TL) / BL
360 NSUM = NSUM + XLD(E)
370 ANXL = NSUM / E
380  NEXT E
390  PRINT "CROSSLINKED DENSITY"
400  FOR F = 1 TO LIMIT
410  PRINT NXL(F)
420  NEXT F
430  PRINT "AVERAGE NO. XLINKS=";ANXL
450  PR£ O: END
1000  REM  DIM MPO(6),MH2O(6),DPO(6)
1110  PRINT "NO. OF SAMPLES FOR DENSITY CALCULATION"
1120  INPUT FINAL
1150  FOR N = 1 TO FINAL
1200  PRINT "MASS OF POLYMER"
1300  INPUT MPO(N)
1400  NEXT N
1500  FOR X = 1 TO FINAL
1600  PRINT "MASS OF WATER DISPLACED"
1700  INPUT MH2O(X)
1800  NEXT X
1900  PRINT "TEMP OF WATER"
```

```
2000  INPUT TEMP
2100 T = 25 - TEMP
2200 DEN = .99707 + T * (2.32 * 10 ^  - 4)
2300  FOR Y = 1 TO FINAL
2400 VPO(Y) = MH2O(Y) / DEN
2500 DPO(Y) = MPO(Y) / VPO(Y)
2600 SUM = SUM + DPO(Y)
2700  NEXT Y
2800 AVD = SUM / FINAL
2850  PR£ 1
2900  PRINT "MASTER MEMBRANE "NAME$
3000  PRINT "DENSITY OF SAMPLES"
3100  FOR A = 1 TO FINAL
3200  PRINT DPO(A)
3300  NEXT A
3400  PRINT "AVERAGE=";AVD
3500  RETURN
```

```
FORTRAN IV      V02.5-3
XLINKS,XLINKS=XLINKS/ID

0001            DO 10 I=1,99
0002            V=0.01*I
0003            A=ALOG(1-V)
0004            B=V*V*0.589
0005            C=-(A+V+B)
0006            D=V**(1/3)
0007            E=V/2
0008            F=147.5*(D-E)
0009            G=C/F
0010            WRITE(5,100)V,G
0011     100    FORMAT(1X,F4.2,1X,F12.8)
0012      10    CONTINUE
0013            CALL EXIT
0014            END
```

```
>RUN XLINKS
0.01  -0.00000006
0.02  -0.00000023
0.03  -0.00000049
0.04  -0.00000083
0.05  -0.00000125
0.06  -0.00000171
0.07  -0.00000222
0.08  -0.00000274
0.09  -0.00000327
0.10  -0.00000378
0.11  -0.00000425
0.12  -0.00000468
0.13  -0.00000502
0.14  -0.00000526
0.15  -0.00000538
0.16  -0.00000534
0.17  -0.00000513
0.18  -0.00000471
0.19  -0.00000406
0.20  -0.00000314
0.21  -0.00000191
0.22  -0.00000035
0.23   0.00000158
0.24   0.00000393
0.25   0.00000674
0.26   0.00001004
0.27   0.00001389
0.28   0.00001834
0.29   0.00002343
0.30   0.00002923
0.31   0.00003579
0.32   0.00004317
0.33   0.00005144
0.34   0.00006067
0.35   0.00007092
0.36   0.00008229
0.37   0.00009484
0.38   0.00010868
0.39   0.00012388
0.40   0.00014056
0.41   0.00015880
0.42   0.00017874
0.43   0.00020048
0.44   0.00022415
0.45   0.00024988
0.46   0.00027782
0.47   0.00030813
0.48   0.00034095
0.49   0.00037648
0.50   0.00041489
0.51   0.00045638
0.52   0.00050118
0.53   0.00054950
0.54   0.00060159
0.55   0.00065772
0.56   0.00071817
0.57   0.00078325
0.58   0.00085329
0.59   0.00092864
0.60   0.00100969
0.61   0.00109686
0.62   0.00119059
0.63   0.00129138
0.64   0.00139977
0.65   0.00151633
0.66   0.00164170
0.67   0.00177658
0.68   0.00192173
0.69   0.00207799
0.70   0.00224629
0.71   0.00242764
0.72   0.00262318
0.73   0.00283417
0.74   0.00306201
0.75   0.00330828
0.76   0.00357474
0.77   0.00386372
0.78   0.00417649
0.79   0.00451663
0.80   0.00488676
0.81   0.00529028
0.82   0.00573117
0.83   0.00621405
0.84   0.00674439
0.85   0.00732872
0.86   0.00797488
0.87   0.00869245
0.88   0.00949324
0.89   0.01039216
0.90   0.01140826
0.91   0.01256656
0.92   0.01390080
0.93   0.01545806
0.94   0.01730694
0.95   0.01955331
0.96   0.02237357
0.97   0.02609665
0.98   0.03145690
0.99   0.04078383
```

Results for the calculation of cross-linked density when $\mu = 0.500$.

>RUN	XLINKS
0.01	0.00000000
0.02	0.00000002
0.03	0.00000006
0.04	0.00000015
0.05	0.00000030
0.06	0.00000053
0.07	0.00000085
0.08	0.00000128
0.09	0.00000185
0.10	0.00000257
0.11	0.00000347
0.12	0.00000457
0.13	0.00000589
0.14	0.00000746
0.15	0.00000930
0.16	0.00001145
0.17	0.00001393
0.18	0.00001677
0.19	0.00002001
0.20	0.00002368
0.21	0.00002782
0.22	0.00003246
0.23	0.00003765
0.24	0.00004343
0.25	0.00004984
0.26	0.00005693
0.27	0.00006475
0.28	0.00007335
0.29	0.00008279
0.30	0.00009312
0.31	0.00010441
0.32	0.00011673
0.33	0.00013013
0.34	0.00014470
0.35	0.00016052
0.36	0.00017765
0.37	0.00019620
0.38	0.00021624
0.39	0.00023789
0.40	0.00026123
0.41	0.00028639
0.42	0.00031347
0.43	0.00034260
0.44	0.00037391
0.45	0.00040754
0.46	0.00044364
0.47	0.00048236
0.48	0.00052388
0.49	0.00056836
0.50	0.00061602
0.51	0.00066704
0.52	0.00072166
0.53	0.00078010
0.54	0.00084262
0.55	0.00090948
0.56	0.00098098
0.57	0.00105744
0.58	0.00113918
0.59	0.00122657
0.60	0.00132001
0.61	0.00141991
0.62	0.00152674
0.63	0.00164100
0.64	0.00176322
0.65	0.00189401
0.66	0.00203400
0.67	0.00218389
0.68	0.00234447
0.69	0.00251658
0.70	0.00270115
0.71	0.00289922
0.72	0.00311192
0.73	0.00334054
0.74	0.00358648
0.75	0.00385133
0.76	0.00413687
0.77	0.00444510
0.78	0.00477830
0.79	0.00513907
0.80	0.00553037
0.81	0.00595563
0.82	0.00641883
0.83	0.00692460
0.84	0.00747845
0.85	0.00808690
0.86	0.00875781
0.87	0.00950078
0.88	0.01032765
0.89	0.01125332
0.90	0.01229689
0.91	0.01348338
0.92	0.01484655
0.93	0.01643352
0.94	0.01831290
0.95	0.02059057
0.96	0.02344296
0.97	0.02719904
0.98	0.03259316
0.99	0.04195489

APPENDIX 4.

Course of Study

L.R.S.C. Electroanalytical Chemistry and Instrumental Analysis.

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